JOURNAL
OF
THE FRANKLIN INSTITUTE
DEVOTED TO SCIENCE AND THE MECHANIC ARTS

VOL. CLXXVII MARCH, 1914 No. 3

PETROLEUM AND ITS DERIVATIVES.*

DAVID T. DAY, Ph.D.,

In Charge of Petroleum, Division of Mineral Resources, Department of Interior.
U. S. Geological Survey, Washington, D. C.
Member of the Institute.

IT will be the purpose of this lecture, first, to familiarize you with such phases of the petroleum industry as may now seem obscure. Then, with a clearer conception of these fundamental matters, we can note how in these later years we are rapidly going further and actually varying the products obtainable from oil as it comes from its reservoirs deep in the earth. This will also suggest lines of investigation by which petroleum products may be transformed into the essentials of life should agricultural products fail.

Research.—Those who are simply interested broadly in petroleum will, I trust, take away from this lecture the conviction that petroleum can be manipulated in many novel ways, that it can at least be made to yield a vast number of useful products. Finally, my own faith permits me to offer you the hope that coal, sawdust, or other low-grade carbonaceous material may be converted into our most essential products by change first into petroleum—this complicated mother substance to which we are surely to look in the future for many of our supplies—and you will not be disappointed.

* Presented at the stated meeting held Wednesday, December 17, 1913.

[NOTE.—The Franklin Institute is not responsible for the statements and opinions advanced by contributors to the JOURNAL.]

Copyright, 1914, by THE FRANKLIN INSTITUTE.

To those of you who are concerned with petroleum investigation I wish to appeal for coöperation in bringing these developments to pass. The time is propitious for organization in petroleum research.

Origin.—The most mysterious problem in regard to petroleum is that of its origin. This is also the problem of least immediate importance to the practical development of the subject.

The reason we actually know so little about this question is because one can count on the fingers of one hand the actual experimental investigations which have been carried on to determine the origin of petroleum, while no one could state off-hand the number of learned men who have occupied volumes with ingenious theories in the hope of settling this question by the speculative method.

There are a few scientific workers who firmly believe that the source of petroleum has been absolutely settled. They go further and state the steps by which one process after another has transformed the original material into petroleum as we find it.

The rest of the scientific world is in a more fortunate condition of doubt—fortunate because in this doubt it is necessary to experiment, and to experiment is to add to our store of knowledge concerning petroleum itself.

Two reasons make the study of the origin of petroleum really worth while: First, we want to know whether the sources of supply have been sufficiently great to predict vastly greater amounts of petroleum in the earth than have yet been discovered. Second, we wish to know whether materials exist for furnishing more petroleum, or whether the ancient stores are all we may ever draw upon.

Petroleum is spoken of as "organic" and "inorganic" by the partisans of the different theories of origin.

By "organic" they seem to mean *derived from material once the product of life processes,* such as plants and animals. No one will doubt that petroleum as it exists is an inorganic mineral substance, because the processes by which petroleum has been formed, no matter from what sources, are evidently inorganic, and no one would confuse the oil which we call petroleum with the oils obtained by organic processes, such as the oils of animals and plants.

The theories advanced by the inorganic and by the organic

groups of speculators concerning the origin of oil are plausible and interesting.

The Inorganic Idea.—The general idea of inorganic origin calls attention to the earth as once a mass too hot for any element to exist in combination with another.

Accepting this idea, we know, by the experience with the electric furnace, that when the earth cooled sufficiently for elementary bodies to combine, compounds of metals with carbon,—*i.e.*, "carbides,"—are among the first to form. They can exist at higher temperatures than other compounds.

As the earth cooled still further, other combinations were possible, such as hydrogen with oxygen.

We can think, then, of a primitive "carbide earth," and, as this cooled, water existing as steam in the atmosphere gradually attacked the carbides with the formation of hydrocarbons, including petroleum, which escaped into the air. After such action the earth consisted of the oxidized crust, and a carbide interior would be acted upon more and more slowly, and water penetrating through the crust would, being in smaller amount, first attack those carbides which are more easily decomposed. Occasionally masses of more refractory carbides, such as carbide of iron, carbide of aluminum, etc., would be passed by. Thus sporadic masses of such refractory carbides might remain until modern times when changes in the earth's crust had provided reservoirs covered with relatively impervious material where our present deposits of petroleum might accumulate.

According to this theory, these processes may still progress.

One of the few experimental investigations as to this theory has been carried out recently by Mr. George F. Becker, United States Geological Survey. He has shown that ammonium chloride, a common constituent of volcanic emanations, when acting upon natural masses of iron, yields its chlorine to the iron, while the hydrogen of the ammonium chloride unites with the carbon in the iron to form petroleum. He has so acted upon natural iron carbide, found in the earth, as to actually make petroleum by such means. In fact, this process can be easily illustrated to you.

Mr. Becker has also called attention to the fact that where deposits of petroleum are known there the deviations of the magnetic needle are greatest. The association of petroleum with

magnetic material, practically iron or magnetite, seems much too close to be accidental, and it may indicate that an important part of the oil is derived from iron carbides; but Mr. Becker does not commit himself to any exclusive theory.

Organic.—By far the greater number of geologists and petroleum chemists prefer the theory that petroleum has been formed from the various residues of animal and vegetable life, stored in very large quantities in the sedimentary rocks where accumulations of oil are found. These scientists have differed very greatly as to the processes which have transformed organic residues into oil. Prof. Carl Engler and his scientific associate, Prof. Hans Höfer, are convinced that they have followed out the detailed steps of the process. In brief, they believe that in the ordinary processes of animal decay, taking place under ground, the portions consisting of fats remain after the rest of the organism has entirely disappeared. These fats are hydrolized, and the fatty acid portion loses oxygen and becomes oil. The different oils result both from varying original materials and from the varying degrees of heat and pressure by which the material has been distilled, with oil as the end product.

Other scientists do not adhere to so detailed a conception of all the stages of oil formation. Mr. David White, of the United States Geological Survey, has formulated exceptionally clearly the view quite generally held among scientific men. This theory is clear, logical, and consistent. First, by the aid of bacterial fermentation—a biochemical process—the plant and animal *débris* is partially disorganized, with the formation of new compounds, the decomposition being interrupted at some stage short of complete destruction. Second, by geochemical and geodynamic agencies the buried *débris* is compressed and subjected to a process of distillation which gradually alters the organic substance and drives off volatile matter. When the organic *débris* consists of peat of ordinary types, or of scattered *débris* of vascular types of plants, the organic deposits are transformed to coal or carbonaceous matter in the shales or sandstones, etc. When the organic *débris* consists largely of resinous and waxy plant products, such as spore covers, seed coats, etc., deposited in comparative purity, the geodynamically and geochemically altered material (much volatile matter being evolved) forms canneloid coals, such as cannel coal, and when the original organic *débris* contains much

algal matter, or matter supposed by most paleobotanists to be algæ, mixed with other plankton material in the muds,—that is, when the deposit is "sapropelic,"—the partially-altered residues are oil shale, oil rock, boghead, etc. In all these cases the material, whether coal, oil rock, or boghead, is already dynamochemically altered and partially distilled, some of the volatile matter (gases and oils) having already been expelled. The kinds of volatile matter depend on the geological conditions prevailing in each case, and the amount of the volatile and the extent of the reduction ("carbonization") of the residues depend primarily on the energy and duration of the dynamic action, though varying according to the kinds of original *débris* of plants and animals. Gases are evolved in all cases, and are still being given off in many coal fields. Oils are believed to be produced by the natural dynamochemical distillation of cannel-forming *débris,* though the more distinctly "sapropelic" matter is supposed to include the principal substances from which petroleum is distilled in the earth.

In some cases these layers of sapropel apparently have become indurated into layers of shaly material which is still in condition to yield oil when under pressure.

Whether our bituminous shales have thus originated or whether they owe their organic matter to infiltrations is a point which may soon be cleared up.

How long the organic matter remains as sapropel before being converted into oil is questionable, but in my judgment the greater the proportion of the total period given to the first stage and the shorter the period assigned to the petroleum after actual formation, the more probable the theory.

At this point I would like to express my lack of faith in the conservatism of the statements frequently made that oil has actually been found in process of formation from seaweed on the surface of water. Scientific accuracy seems to be entirely lacking for these obviously improbable observations.

However the organic matter may have been converted into petroleum, we recognize that the oil was at first scattered in minute drops through the earth, and these gradually collected, largely driven by the superior capillary action of water into such porous rocks as can serve as good repositories, and where the oil is confined by comparatively impervious rocks—usually clays or shales

with their capillaries filled with water. During this process of accumulation it is quite possible that the character of the oil has essentially changed. Thus oils which have penetrated into shales are found to be simpler in their make-up than those in other rocks, such as limestones. It would seem from what we find that the shales have taken out part of the original constituents, and I have proved it possible to abstract certain parts of oils merely by diffusing these complex oils through dry clay.

How Our Various Oils are Utilized.—We can think of the petroleum which is produced in the West as all containing more or less of Pennsylvania oil, with greater or less admixture of asphalt, and, in the case of California oil, considerable proportions of members of the coal-tar series.

For a long time these Western oils were not taken at all seriously, inasmuch as the supply was abundant of Pennsylvania and West Virginia oils. Moreover, the Western oils,—that is, of Texas and California,—were very difficult to refine. A process was soon found for refining Texas oils, but the California oil remained a problem. While it was easy to remove the asphaltic material, the coal-tar oils, such as benzol, toluol, etc., distilled over with the illuminating oil and made it burn with a smoky flame. One of the chemical engineers of the Standard Oil Company of California found, however, that fuming sulphuric acid,—that is, sulphuric acid containing sulphur trioxide in solution,—has the property of taking out these coal-tar oils quite completely, and furnishing a very satisfactory kerosene. With this discovery the refining of California oils progressed rapidly in spite of the fact that in distilling off all the available kerosene the total proportion obtained was comparatively small. This difficulty of extracting coal-tar hydrocarbons from petroleum has been met with to even greater extent in Roumanian oils, and there a still more modern process has been applied, though too recently for an estimate of its practical value. By this the distillate containing coal-tar oils is treated with liquid sulphur dioxide, which extracts the coal-tar oils in preference to the paraffin hydrocarbons, and thus renders the latter suitable for lamp oils. This ingenious process, moreover, admits of separating, finally, the coal-tar oils in a condition suitable for use, whereas they are practically destroyed when separated by means of fuming sulphuric acid. Thus to-day there are no varieties of crude petroleum

in the United States which cannot be refined satisfactorily, although the yields of refined products in the West are by no means so great as with the Eastern oils.

Heavy Texas and California oils can also be made to yield very satisfactory lubricating oils. A process is under way which probably will give considerable yields of paraffin wax, even from California oils, in which, naturally, almost no paraffin wax is present.

The amount of oil refined and the amount used for other purposes are now merely questions in the United States of a market for the resulting products. If all our oils were used in the United States and not exported, the oils of the East and of Oklahoma would be an abundant source for all the desired kerosene, and perhaps gasoline as well, but about one-fifth of all our oil is exported in one form or another, especially kerosene.

As each year goes by, technologic improvements in the treatment of petroleum make this material more flexible for suiting all market demands, so that in general it may be said that enough oil is refined to meet the foreign and domestic demand, first, for kerosene and gasoline; then attention is given to the much smaller and more easily satisfied demand for lubricating oils; and, finally, to the ever-increasing demand for paraffin wax.

The rest of the product can always be gotten rid of at fairly lucrative prices for fuel oils. In fact, the price for fuel oil has almost doubled in the last five years.

In general, all of the Eastern oils are refined to the greatest possible extent, producing gasoline, kerosene, lubricating oils, paraffin wax, and a minimum of gas oil and fuel oils. In fact, it is the common practice to distil these oils entirely to coke with a production of practically no fuel oil.

As these oils are insufficient for the distillation needs of the country, large quantities of oil from Ohio, Indiana, Illinois, and Oklahoma are similarly refined to the utmost limit. The same is true of the oil from the Caddo (Louisiana) field and from the Electra region in northern Texas, where the oils are of Pennsylvania grade. Meantime the oils of Texas are largely used for fuel purposes, though a certain amount is sent in tank steamers to the Eastern States, or worked up at Port Arthur, on the Texas coast, for the production of superior lubricating oils.

Since all this does not suffice for the foreign and domestic

demand for refined products, Wyoming is called on for similar use of its light-grade oils, the production of which is increasing very rapidly in the Salt Lake field near Casper.

These oils above mentioned, comprising our total supply, apart from California, amounted to about 135,000,000 barrels in 1912, while California yielded 87,000,000 barrels more. This California contribution is the really flexible quantity. It can be used in so far as necessary for refining purposes, but principally as a great source of fuel oils and for road asphalts. This supply of fuel oil will enter significantly into Eastern commerce with the opening of the Panama Canal.

Since this lecture was prepared the United States Geological Survey has pointed out the existence of very large bodies of oil shales in Colorado and Utah which are richer than the Scottish oil shales. Some will yield two barrels of oil per ton by distillation, while the usual oil-bearing sands yield less than half that much. Shales yielding 30 gallons per ton of crude oil probably exist, according to estimates of Mr. E. G. Woodruff, of the Geological Survey, capable of yielding *15 billion barrels* of crude oil.

Imports.—Two other sources add to the total oil supply of the United States; namely, considerable imports of heavy Mexican crude oil, suitable principally for road asphalt and fuel oil. This Mexican importation will undoubtedly steady the price of fuel oil in the next year, as some twenty of the largest tank steamers afloat have been built for this trade and will bring large quantities to the Eastern ports. The second source is light distillate, yielding large proportions of gasoline and coming from Borneo and Java to Pacific ports. Thus while we are exporting gasoline on the Atlantic Coast we import it on the Western shore.

Our Relation to the Rest of the World.—The total production of petroleum in the United States is now, roughly, 240,000,000 barrels. This means two-thirds, and more, of all the petroleum produced in the world. And yet the first commercial development of significance took place barely half a century ago. There is now no sea whose waters are not churned by the propellers of oil-burning steamships, no country whose roads have not seen the gasoline motor car, and no village in the civilized world in which the flame of kerosene or some form of petroleum does not illuminate some house, and thousands of miles of highways are kept free from dust or otherwise improved by petroleum oil.

We owe our standing in national intelligence to the light of the kerosene lamp. We owe our greatest industrial characteristic —flexibility in manufacturing processes—to the national habit of reading. Kerosene light has been cheap, and is cheaper in the United States than anywhere else, and it has prevented all other lights from following the high price of living.

Foreign Ownership of American Oil.—Petroleum has had its share in developing American prestige. It has done more than precious metals or precious stones. Probably more people have used kerosene than have ever seen a gold coin. The petroleum and natural gas produced last year outvalued our gold, silver, lead, zinc, and all other metals combined, except iron and copper.

I offer these quantities merely to stimulate the natural inquiry as to how we are administering this trust of national, natural advantage: an advantage over less favored nations which it is a pledge of our patriotism to maintain. Are we maintaining it to the best purpose?

We are not. In no line of national conduct is the progress so recklessly devoid of any thought-out policy. Besides a system of production which considers neither supply nor demand at home, we squander our heritage over the face of the earth, and we do worse. It may well be claimed as good public policy that our oil should spread out to less favored lands as the handmaid of education where it will do the greatest good, and to this we must subscribe. No missionary can compete with the lamp, nor work without a lamp. But what policy broader than dollar greed can defend the sale of our greatest single weapon for national independence, our oil lands themselves, to foreign capitalists, if not to foreign nations?

Sir Marcus Samuel spoke in regard to this at the annual shareholders' meeting of the Shell Transport and Trading Company, Limited, in London, October 10th. The speech was given wide publicity in the English press.

The Shell Transport and Trading Company, Limited, is an important part of the immense petroleum combination of Europe, known as the Royal Dutch-Shell group, dominated by the Deutsche Bank and the Rothschilds.

Sir Marcus Samuel said, among other statements:

"The business is world-wide, and we are determined that the great distributing organization which we have created shall

not be dependent upon any one field, or upon any one country, or upon any one government. We shall endeavor to acquire oil territories, so essential to the support of our organization, wherever they can be found.

"It is mainly in pursuance of this policy that we have purchased the 'Californian oil fields.' It is in connection with that purchase that we are providing the large sums that we have asked you to subscribe.

"The business which we have obtained has been managed upon lines which commend themselves to us. From time to time properties have been purchased to strengthen the reserve of territory. The oil produced is among the very best obtained in California. We are satisfied that it is going to prove an excellent investment at the price we have paid for it, which was £400,000 in Shell ordinary shares and £400,000 in cash, 60 per cent. of which is provided by the Royal Dutch.

* * * * * * *

"The position of the companies in Roumania and in Russia continues highly satisfactory. In both countries we are the largest producers.

* * * * * * *

"In Mexico we have acquired, over carefully chosen territory, large areas at small cost.

* * * * * * *

"Borneo continues to show its extraordinary riches. It is the possession of that field which enables us to enter into contracts which we certainly would not commit ourselves to do without it. The wisdom of your directors in consolidating the interests of your company with those of the Royal Dutch Petroleum Company is proved constantly and daily.

* * * * * * *

"Other subsidiaries in which we are interested, and on which we have options on considerable blocks of shares at very much below current quotations, are doing well, and promise to increase the company's earnings."

* * * * * * *

The facts are open to every one, but recognized by few, that 25,000 barrels a day, over 12 per cent. of the oil in Oklahoma, are produced by foreign companies, and the foreign ownership in California is increasing even faster.

The chief significance of this is that practically every foreign power is adopting oil in place of coal for its battleships, and a supply of oil is requisite for this purpose.

There is no opportunity here to develop a policy, but there is an opportunity for directing thought, and I bespeak the influence of this time-honored institution, developed within the sound and in the spirit of our national Liberty Bell, in giving sympathy and counsel to our national government as to these problems when developing petroleum legislation.

Supply of Gasoline.—This consideration naturally suggests the vital question of an adequate gasoline supply. Even if we produce 25,000,000 barrels of gasoline in the next year, this would probably be too little for a year or two of further automobile progress.

The means for meeting the demand are in sight.

This answer is far easier to state than to explain. In the first place, recent developments in knowledge of the resources of the United States make it probable that there will be no great decline in oil production in the near future, therefore no *decline* in gasoline supply is likely. As to the necessary increase: this will come from synthetic gasoline obtained from petroleum itself. To make this clear, it is necessary to refer in great detail to the nature of petroleum. We know that this long series of oils which mixed together constitutes petroleum begins with oils which boil more easily than ether, and each following one in the series boils at a higher temperature. By distilling out those which boil below 300° F. we obtain from Pennsylvania oils about 20 per cent. of so-called naphtha. By redistilling this we obtain gasoline, but the naphtha itself is fairly suitable for automobiles. The mid-continent oils yield slightly smaller proportions of gasoline. The oils of northern Louisiana and Texas yield as much as Pennsylvania. The gasoline yield from the Gulf Coast of Texas and Louisiana and from California is very much less, so that at present the West coast is practically left out of consideration, and its gasoline is supplemented by importation from the Orient.

Cracking.—After the natural yield of gasoline has been taken from crude oils, the remaining portion boils at too high temperatures to be suitable for automobiles, although the higher-boiling kerosene is used successfully under exceptional conditions which cannot be considered here. Therefore the limit of gasoline would

seem to be reached—were it not for the fact that many oils break up into lighter oils when heated.

Thus, certain Mexican petroleums contain naturally only 2 per cent. of gasoline, but, by slowly heating, these oils break up so that they yield about 7 or 8 per cent. of gasoline. But these so-called "cracked" oils are bad smelling and difficult to refine. Several years ago I found that if these oils are distilled under pressure the yield of gasoline is still greater, and that the unpleasant odor due to deficiency in hydrogen in the composition of the oils can be remedied by actually combining hydrogen with the oil in the still under the influence of a catalytic agent. Recently the demand for any kind of gasoline has waived the requirement of good odor, and other processes are producing much synthetic gasoline. By such means low-grade residues have been made to yield from 20 to perhaps 70 per cent. of their weight in material which will serve as gasoline.

The Study of Individual Hydrocarbons.—The main difficulty in carrying out these processes is lack of knowledge of the behavior of individual oils when heated. At this point our fundamental study of individual hydrocarbons fails. It seems wise just at this time to encourage to the greatest extent the study of the characteristics of these individual hydrocarbons—not only to know more of the way they break up when heated, but to study the effect of chemical agents upon them in forming a long series of new substances and of old substances in cheaper or purer conditions.

To this plea for greater exactness of knowledge I would ask your earnest attention.

Nature of Petroleum.—But what are complex and what are simple oils? What is petroleum? Petroleum is so many things under so many conditions that at first it seems hopeless to attempt to define it.

Yet we can distinguish between petroleum and all other substances as being made up of hydrocarbons and frequently holding in solution those indefinite compounds of hydrogen and carbon, with oxygen or sulphur, or both, that we call asphaltic compounds.

There are so many hydrocarbons interdissolved in this complex mixture, usually containing different proportions of hydrogen to carbon, that they would seem to grade without solution of continuity from marsh gas through hydrocarbons containing

progressively more carbon. Meanwhile, blended with these pure hydrocarbons are, frequently, the asphaltic materials, which, with ever-increasing carbon, extend the complexity of the subject through gilsonite and grahamite to the indefinite border land of coal.

We recognize that a separation of this great mixture into all its simple oils is beyond the possibility of any one man, and—to further present, frankly, the sum of discouragement which this problem presents—while we are separating these constituents, many of them are broken up into still new oils by the very agents (heat, chemicals, etc.) which we use for their separation.

In spite of all this, the work of many scientists taken together has isolated one oil after another and simple individual oils have been taken out of the mixture. We all know that this has taught the encouraging fact that there is system in the variation of these oils one from another. We know that we can group the oils into a few homologous series, and in each series each oil differs from the next member by a definite amount of hydrogen and carbon, and with a difference in boiling-point which makes possible certain methods of separation. There is similar difference in viscosity, specific gravity, etc., which properties are also being availed of as aids in separation.

It is only recently that we have come to avail ourselves of properties which characterize each series as a whole in order to separate a whole group at once and then study its members.

Group Separations.—The first of these processes, historically speaking, has been to treat the complex oil with sulphuric acid, and by keeping the acid cold and using it sufficiently strong we can destroy and thus remove all of the groups except what we call paraffin hydrocarbons, and if we heat the oil we can easily attack these paraffin oils also. Lately other important processes have been added: thus Nastukoff in Russia has found that by treating oils with formaldehyde and sulphuric acid, condensation products are formed with certain groups of oils. Again, Holde and others have formulated methods for extracting certain kinds of asphalt from oils by precipitation with gasoline. These and other methods which it would lead us too far to consider have enabled Professor Engler to formulate a general method which it is believed will soon enable us, for purposes of study, to sufficiently separate a given petroleum into its groups of components,

and the study of each of these will soon give far better fundamental information of the constitution of our oils. Evidently many surprises await us as to the character of these individual oils. We are accustomed to think of the best of oils as having odors that are persistent and disagreeable. These we will find are due usually to slight amounts of impurities. Already we know odorless oils such as albolene and vaseline when fresh—that qualification "fresh" is significant and of promise. The very fact that oils develop an objectionable odor with age is significant when we learn that these odors are chiefly oxidation products allied to fatty acids, and of the greatest promise for the future production of such valuable substances as butyric, oleic, stearic, and other acids. We must look upon the individual petroleum oils, therefore, as the starting point for compounds of great utility. The greatest advance which has come in the consideration of the chemical derivatives from these oils is due to recognizing that these hydrocarbons are, after all, not the refractory inert substances that we have taken them to be, but susceptible by chemical treatment of yielding a host of products. Theoretically, this has long been possible—as a practical feature it is in its infancy. But already the oxidation products, such as fatty acids capable of being saponified into soaps, are being investigated in this city. Chlorine products are being made which offer strange new properties with suggestions of many new uses. Strangely enough, these chlorine products will not burn readily, and already some of these products of inflammable kerosene are used most effectively as fire extinguishers.

Improving Oils by Adding Hydrogen.—Another line of investigation is proving helpful in the direction of adding hydrogen to oils which owe their bad odor and color to lack of saturation. The chemical possibilities with these lower grade unsaturated products are problems for the future. We know at least that we can add hydrogen to them and then form the chlorine or oxygen products which have already been referred to, but beyond doubt their unsaturated condition will enable them to be acted upon directly to form other lines of valuable products. In fact, years ago, my brother, Dr. W. C. Day, then of Swarthmore College, indicated a line of valuable research by actually making good varnishes by treating waste unsaturated residues with nitric acid. We know little of what sulphur will accomplish in combination

with oils. The same is true of phosphorus and other active chemical agents. The very vastness of this field of research teaches one fundamental lesson, one suggested by the coal-tar industry. It is characteristic of that industry that the individual oils were easily separable from each other, so that the fundamental properties of each could be thoroughly studied once for all, and upon that basis of thorough and exact knowledge vast stores of useful application were quickly based, yielding us, besides aniline dyes, saccharine and a host of helpful medicines. But we have no such fundamental knowledge of petroleum oils. Can there be any doubt that the quickest, surest road to the knowledge of the chemical uses for petroleum for the most successful application of it in all ways must be by promoting the study of the individual components? Such exact, purely scientific, work must be carried out by an organized corps of workers supported by an endowment for this work, and be purely fundamental and kept distinct from industrial work, or it will prove too complicated for prompt completion. It is the work of many, but it may be begun by one—some one capitalist who will benefit all mankind by a foundation for petroleum research.

Salt in British Columbia. ANON. (*Mining and Eng. World*, Oct. 25, 1913.)—An extensive bed of salt has been discovered at Kwinitsa (mile 45, on Grand Trunk Pacific Railway), on the Skeena River. Up to the present five holes have been drilled, some more than a mile from others, and all have struck salt, at depths varying from 50 to 250 feet. About eight tons have been taken out. The principal salt wells of Canada are situated in Western Ontario. On account of the long rail-haul, most of the salt used in British Columbia is imported from California. The presence of salt beds near Vancouver is, therefore, of importance.

The Influence of Foreign Substances on the Activity of Catalysts. C. PAAL and A. KARL. (*Ber.*, xlvi, 3069.)—It has been previously shown that the activity of palladium as a catalyst in hydrogenations was remarkably diminished when it was deposited on aluminum, iron, copper, silver, tin, or lead. It is now shown that the oxides, hydroxides, and carbonates of these metals behave in a similar manner. Basic lead carbonate entirely prevents hydrogenation, while zinc oxide, zinc carbonate, aluminum hydroxide, and ferric hydroxide greatly reduce it. Cadmium carbonate is also an anti-catalyst. On the other hand, magnesium oxide, like metallic magnesium, does not reduce the catalysis, but rather, on account of its greater surface, increases it.

Ductile Tungsten. C. G. FINK. (*Amer. Electrochem. Soc., Trans.*, xxii, 499.)—This article deals with the various applications of the metal in particular as a substitute for other more expensive or more easily corrodible metals. *Electrical Contacts.*—Wrought tungsten can successfully replace platinum and platinum-iridium alloys for contact points in spark coils, relays, etc., and, owing to the greater hardness, higher heat conductivity, and lower vapor pressure of tungsten as compared with platinum, the life is longer. Tungsten gauze is recommended for use in various chemical processes, while tungsten anticathodes for X-ray tubes are said to be more efficient than those of other metals. *Thermoelectric Behavior.*—The electromotive force of a tungsten-molybdenum couple increases with temperature up to about 540° C. (12½ millivolts), then decreases and passes through zero (millivolts) at about 1300° C.; this couple serving as a convenient measure of high temperatures in the tungsten-hydrogen furnace. *Standard Weights.*—Owing to its high density, 19.3 to 21.4, its indifference to atmospheric attack, and the fact that it can be made hard enough to scratch glass, tungsten is a suitable material, and the weights are said to remain wonderfully constant. *Suspensions and Micrometer Wires.*—Sizes down to 0.0002 inch have been drawn, and are well adapted for galvanometer suspensions, cross-hairs in telescopes, and for surgical uses, in place of the coarser gold and silver wires. Musical instruments might also be provided with tungsten wires in climates where steel is readily corroded. It is also suggested that it could advantageously replace phosphor-bronze in many cases.

Photo-electric Behavior of Iron. H. S. ALLEN. (*Faraday Soc.*, Nov. 12, 1913.)—Iron which is chemically active shows a relatively large photo-electric activity,—*i.e.*, it loses a negative charge fairly rapidly when insulated and illuminated by ultraviolet light. Processes which render the iron passive greatly reduce this activity. These facts are in good agreement with the theory that the cause of passivity is the presence of a gaseous layer at the metallic surface. This theory, like the oxide-film theory, was originally advanced by Faraday.

New Electric Pendulum. M. SCHANZER. (*Zeitschr. Instrumentenk.*, xxxiii, 218.)—This describes a new form of apparatus for electrically maintaining the motion of a pendulum. The energy consumption is very small, only 8 milliwatts; and the ratio of the length of arc during which the pendulum is driven, to the whole swing, is about 1 : 18, the pendulum thus swinging freely for the greater part of its motion. The pendulum itself is a quartz rod, 110 cm. long and 1.8 cm. diameter, so that there is only a small variation of length with temperature. The whole apparatus can be enclosed, so that the pendulum can swing *in vacuo* if required. The original paper gives diagrams and details of the mechanism.

RESISTIVITY OF PURE GOLD IN TEMPERATURE RANGE 20° C. TO 1500° C.*

BY

EDWIN F. NORTHRUP, Ph.D.,

Member of the Institute.

In obtaining data for tracing the resistivity of pure gold from 1500° C. to below its freezing point, the method and apparatus employed were in all essential respects the same as were used in the measurements of copper, which were fully described by the writer in the JOURNAL OF THE FRANKLIN INSTITUTE for January, 1914. A full description of the furnace used may be found in *Metallurgical and Chemical Engineering*, January, 1914.

The gold used in the measurements was purchased from Baker and Company, Inc., Newark, N. J. In making the purchase it was requested that gold of the greatest obtainable purity should be furnished. The Baker Company wrote that they would prepare and ship "the chemically pure gold wire as covered by your specifications." No analysis of the gold was made to determine if these specifications had been met. The resistivity, 2.316_6 at 20° C., is fairly low and shows that the gold must have been at least approximately pure.

The containers for the molten gold were constructed in the same manner as those used for copper, but the dimensions were changed in certain respects. The diagram Fig. 1 shows the dimensions chosen for gold container No. VI. It will be noted that the potential terminals join the current circuit only 1.5 c.m. above the lowest part of this circuit. Experience shows that the length of the channel of molten metal being measured is quite sufficient for adequate sensibility, and by choosing the point where the potential holes join the current circuit low down, the temperature can be made almost exactly uniform over the portion of the circuit the resistance of which is measured.

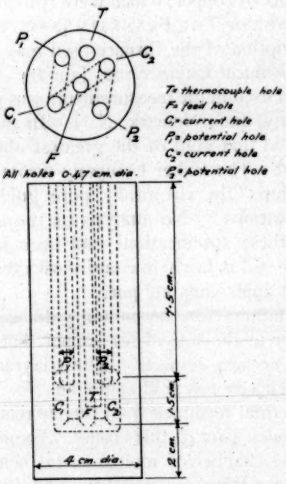
Further experiments indicated that a better proportion, than formerly used, of alundum and magnesite for making the containers is: magnesite 45 parts and alundum 55 parts. These proportions are now adopted for all this work.

A method was devised for tracing the resistivity of the gold

* Communicated by the author.

in the solid state from 20° C. to its melting-point which proved to be accurate and very easy to apply. It was carried out as follows: The gold was in the form of wire 0.101_3 cm. diameter. The resistivity of this wire at 20° C. was determined in an oil bath, by the method of the Kelvin double bridge, and found to be 2.316_6 microhms per centimetre cube. This same gold wire was wound into a helix about 1.5 cm. long, with the turns well separated. The diameter of the helix was such that the end of a porcelain tube about 0.5 cm. in diameter would pass into it. The porce-

FIG. 1.



lain tube contained the thermocouple. Gold wire potential leads were electrically welded to the gold wire near each end of the helix. Over the four terminals thus formed porcelain tubes were slipped to electrically insulate the leads from each other. The arrangement so formed was put on the inside of a large quartz tube and centrally located in the furnace chamber. The four gold wire terminals, two current and two potential leads, passed through small holes in the baked lavite-cover piece of the furnace. It was now possible to determine the resistance by means of the Kelvin double bridge of the helix of gold wire between the

points where the potential terminals were attached and, at the same instant, to read the electromotive force of the thermocouple with a potentiometer. By slowly heating the furnace, 31 points for a curve relating resistance and temperature were obtained. The last reading was at a temperature of 1070° C., when the circuit completely opened from the melting of the wire. Indications of a change of resistance began at 1063° C. It is probable that the surface tension of the wire preserves the circuit for a short time after fusion begins.

Having the resistance values from 20° C. to the melting-point of gold, and knowing the resistivity at one temperature, the constant could be calculated by which all resistance values must be multiplied to obtain resistivities for corresponding temperatures. The points for the curve as plotted in the solid state were obtained in this way.

The thermocouple, used in all the gold measurements, was a platinum *vs.* platinum + 10 per cent. rhodium couple, encased in a glazed tube of Royal Berlin porcelain. This thermocouple was calibrated by the writer by using the melting-points of different metals for giving fixed temperatures. The method which the writer has found most convenient for calibrating a couple in this way is the following: The metal to serve for the fixed temperature, pure nickel for example, is selected in the form of wire, about No. 22 or 24. This wire is doubled on itself and one half of its length is insulated from the other half with small-bore porcelain tubes. The doubled wire is mounted in a larger porcelain tube exactly as one would mount a thermocouple. This tube and the tube of the thermocouple to be calibrated are laid together and placed in the furnace. A storage cell, 5 ohms resistance, and a buzzer are connected in series. The two ends of the wire, which is to give the fixed point of temperature, are joined to the terminals of the buzzer, which thus becomes shunted so long as the wire is intact. The instant the wire melts the buzzer sounds, at which moment the electromotive force of the thermocouple is read with a potentiometer. If the furnace has a large chamber, various wires, as tin (232° C.), cadmium (320.2° C.), silver (960° C.), gold (1062.4° C.), copper (1082.6° C.), nickel (1452.3° C.), and palladium (1549.2° C.), may be mounted, each in a separate tube, and all these tubes, together with the thermocouple tube, can be bound together in a bundle, their ends coming to the same

level, and be mounted in the furnace. The temperature may be raised slowly and the electromotive force of the thermocouple read at the instant each metal melts, as the temperature is raised. This is the general plan which the writer adopts for the calibration of his thermocouples.

After the experience, acquired in the measurement of copper and other metals, it appeared entirely practicable to expect to have independent determinations of the resistivity of gold, in the neighborhood of 1200° C., to agree to better than 0.25 of 1 per cent. This expectation has been realized in the case of gold. For example, under similar conditions of slow cooling, the resistivities obtained in the measurement of December 20, 1913, at 1218° C. and 1140° C., were respectively 33.00 and 32.00 microhms, container No. V being used, and the resistivities obtained in the measurement of January 10, 1914, at 1217° C. and 1140° C., were exactly the same, container No. VI being used. The writer has considered that all determinations of the resistivity of pure metals in the liquid state should be made at least twice, using a different container having a different constant for each determination. When this is done and the agreement is close, one's confidence in the precision of the results is secure. As the writer has previously stated, the resistivity of a metal in its molten state is independent of its past physical history, and depends only upon its temperature and its purity. It, therefore, is desirable to be able to measure the resistivity of molten metals with high precision, because of the information which such measurements of precision can give regarding the chemical purity or chemical constitution of the metal or alloy. It is a satisfaction to find that a measurement may be made in which the error is not greater than 0.25 of 1 per cent. when a metal is in its molten state, and with more experience even better results may be expected.

Since the report made on copper the writer has acquired information about a matter of extreme importance connected with this method of measurement. It is this: Unless the material, of whatever nature apparently, of which the container is constructed is fired to a temperature in excess of that to which the measurement is to be carried, the container will evolve impurities which will contaminate the molten metal and permanently change its resistance. In the first measurement of the resistivity of

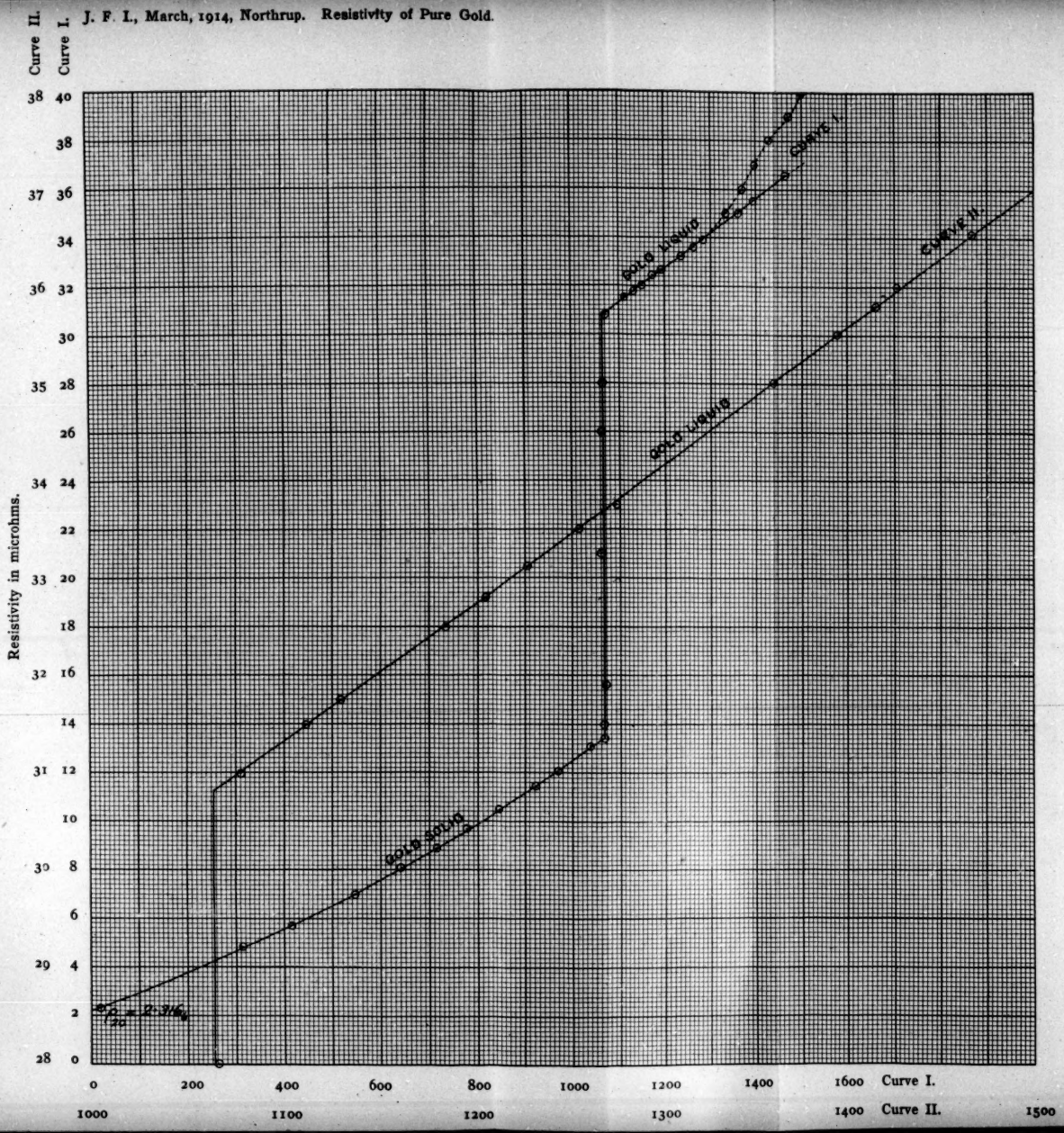
gold in the molten state the magnesite-alundum container used had only been preheated to 1250° C. A glance at the curve (see dotted line) will show that at just about this temperature the increase in the resistivity of the gold being measured was more rapid than a linear relation. If only one determination had been made it would have been wrongly concluded that the increase in resistivity of gold in the liquid state is not linear after 1250° C., and that the resistivity at 1500° C. is 40 microhms, whereas the true resistivity is but 37.2 microhms. As the writer was confident that the more rapid increase in resistance above 1250° C. was due to an increasing contamination of the gold by matter evolved from the container, he prepared in a second determination for an avoidance of this contamination by preheating the second container used to a temperature in the neighborhood of 1600° C. As was expected, the increase in resistivity of gold in the liquid state, as found in the second determination, is strictly linear up to the highest temperature at which resistivity was measured, which was 1467° C.

TABLE I.

Resistivity Values for Pure Gold in Temperature Range, 20° C. to 1500° C.

Degrees Cent.	Microhms per centimetre³	Ratios ρ_t/ρ_{t_1}	Remarks.
20	2.316_8		Gold solid.
300	4.72		Gold solid.
500	6.62		Gold solid.
800	9.94		Gold solid.
1000	12.54	$\frac{\rho_{1000}}{\rho_{20}} = 5.411$	Gold solid.
1063	13.50	$\frac{\rho_{1063}}{\rho_{20}} = 5.827$	Gold solid.
1063	30.82	$\frac{\rho_m}{\rho_s} = 2.28_2$	Gold molten.
1100	31.34		Gold molten.
1200	32.76		Gold molten.
1300	34.17		Gold molten.
1400	35.58		Gold molten.
1500	37.00	$\frac{\rho_{1500}}{\rho_{1000}} = 1.181$	Increase per degree = 0.014142.

The results of all observations taken are embodied in curves. Thirty-one points were observed for gold in the solid state, fifty-three points for gold measured in container called No. V, Decem-


J. F. I., March, 1914, Northrup. Resistivity of Pure Gold.
Curve II.
Curve I.
Resistivity in microhms.
Gold Liquid
Curve I
Curve II
Gold Liquid
Gold Solid
Gold Solid
0 200 400 600 800 1000 1200 1400 1600 Curve I.
1000 1100 1200 1300 1400 Curve II. 1500

ber 20, 1913, and forty-two points for gold measured in container called No. VI, January 10, 1914. It would only lead to confusion to place all these points, many of which fall at the same place, on the curves. Only a few points which are typical are therefore shown. A table of the more important values is given.

The writer is again indebted to his wife for her assistance in taking the observations and working up the data.

He desires to reserve for a later paper comments upon the interpretation to be placed upon the observed facts and his conception of their significance as bearing upon the electron theory of metallic conduction.

PALMER PHYSICAL LABORATORY,
PRINCETON, N. J.

Copper-Covered or Copper-Clad Steel. J. O. HANDY. (*J. Ind. Eng. Chem.*, v, 884–895.)—A brief description of the manufacture, properties, and uses of steel covered with a layer of copper, either by alloying or welding, and including extracts from patent specifications and a bibliography of United States, English, German, French, and Belgian patents on the subject. It is stated that a union capable of withstanding mechanical working can be obtained both by the alloying method, in which the copper is melted, and by welding, when the copper is only rendered plastic by heating, for example to 950° C. Melted copper dissolves iron very rapidly, and since the electrical conductivity of copper is diminished by the solution of iron therein, the welding process is more satisfactory for the manufacture of copper-clad wire. Sheets of copper-clad steel exposed to the moist, acid atmosphere of Pittsburgh showed very little corrosion, even after two years. Copper-clad wire is now largely used, but the use of other forms of copper-clad steel might advantageously be extended in many directions, especially for constructional purposes.

Radio Elements and their Electro-chemical Behavior. F. PANETH and G. v. HEVESY. (*Monats. Chem.*, xxxiv, 1593.)—The chemical identity of certain radio elements with other elements, referred to by Soddy, extends also to their electro-chemical behavior. The decomposition potential of thorium C_1 and radium E is the same as that of bismuth, that of radium D and thorium B the same as that of lead, and that of radium A about the same as that of polonium. The electrolytic separation of thorium C_1 and radium E is for this reason retarded by the addition of bismuth, and that of thorium B by lead, and these facts may be utilized to obtain a more complete separation of radio elements than has been possible hitherto.

THE PRESENT PHYSICAL KNOWLEDGE OF X-RAYS.*

BY

WHEELER P. DAVEY,

X-Ray Laboratory, Department of Physics, Cornell University.

GENERAL PROPERTIES OF X-RAYS.

THERE are certain general properties which are common to all X-rays. Among these are:

(1) The fluorescent effect.
(2) The photographic effect.
(3) The ionizing effect.
(4) The chemical effect.
(5) The action upon a selenium cell.
(6) The penetrating effect.
(7) The physiological effect.

(1) Certain uranium compounds and certain salts of alkali and alkali-earth metals have the property of giving off light when exposed to the action of X-rays. When the intensity of the radiation is increased (as, for instance, by bringing the source nearer) the intensity of the fluorescent light is increased. Röntgen [1] does not find any general simple relation between the P. D. applied to the tube (as measured by the current in the primary of his induction coil) and the amount of fluorescence produced on a screen of barium platino-cyanide, but states that in some cases he has been able to get the two in direct proportion to each other. But with constant conditions of excitation for a given X-ray tube, the intensity of the fluorescent light from the screen always varies inversely as the square of the distance from the screen to the target of the tube.

(2) The action of X-rays upon a photographic plate at a given distance from the tube depends partly upon the current sent through the tube and partly upon the penetrating ability of the rays employed. Other things being equal, an increase in the current hastens the photographic action, while an increase in the penetrating ability of the rays makes it slower. Two X-ray

* Communicated by the author.

[1] W. C. Röntgen, *Wied. Ann. d. Phys. u. Chem.*, 64, 1898.

beams which produce equal effects upon a fluorescent screen do not necessarily produce equal effects upon a photographic plate.[2]

Luther and Uschkoff[3] thought they detected a difference between the action of X-rays upon a silver gelatino-bromide plate and that of light upon the same plate. It is possible that their results may be explained upon the same basis as solarization.

(3) If a gas is exposed to an X-ray beam, it is broken up into ions, or electrically-charged atoms. While the quantity of charge carried by different ions is not always the same, still it is always some exact whole number times 4.9016×10^{-10} electrostatic units of charge.[4] The sum of all the charges carried by all the ions of a given sign is often used as a measure of the quantity of radiation which has produced them. As the sum of all the + charges must necessarily exactly equal the sum of all the − charges it is immaterial which sign of charge is used in the measurement. The amount of ionization produced in a gas in a given time depends upon the inverse square of the distance from the target of the tube,[5] the P. D. applied to the tube,[6] the penetrating ability of the rays,[7] [8] the nature of the gas,[9] the pressure of the gas,[6] [7] [8] but is independent of the temperature of the gas.[9, 10]

(4) Except for the action of X-rays upon the materials in the film of a photographic plate, the only chemical actions so far noticed seem to be a precipitating effect, a dehydrating effect, a hydrolytic effect. Iodine is precipitated from its solution in chloroform by exposure to the rays.[11]

Schwartz has found an ammonium oxalate-mercury bichloride

---

[2] W. C. Röntgen, *loc. cit.*
J. O. Heinze, Jr., *Amer. Jour. Sci.*, 13, pp. 313–314, April, 1902.

[3] R. Luther and W. A. Uschkoff, *Phys. Zeitschr.*, 4, pp. 866–868, Dec. 15, 1903.

[4] R. A. Millikan, *Science*, 32, pp. 436–448, Sept. 30, 1910.

[5] E. W. B. Gill, *Phil. Mag.*, 23, pp. 114–121, Jan., 1912.

[6] W. Hillers, *Wied. Ann.*, 68, 2, pp. 196–232, 1899.

[7] R. K. Mc Clung, *Phil. Mag.*, 7, pp. 81–95, Feb., 1904. *Nature*, 69, pp. 462–463, March 17, 1904. *Phil. Mag.*, 8, pp. 357–373, Sept., 1904.

[8] C. G. Barkla, *Nature*, 80, p. 187, April 15, 1909.

[9] J. A. Crowther, *Camb. Phil. Soc. Proc.*, 15, pp. 34–37, Feb. 23, 1909. *Roy. Soc. Proc.*, Ser. A, 82, pp. 103–127, March 10, 1909.

[10] J. H. Clo, *Astrophys. Jour.*, 33, pp. 115–124, March, 1911.

[11] H. Bordier and J. Galimard, *Arch. d'Elec. Med.*, 14, Aug. 10; Sept. 10, 1906.

mixture which precipitates calomel under the action of X-rays.[12]

Ammonium, potassium, barium, and magnesium platinocyanides change color when exposed to X-rays, due to dehydration.[13]

When starch is exposed to the rays it is changed into soluble starch and then into dextrin.[14]

(5) X-rays affect the electric resistance of a selenium cell in the same manner as light.[15]

(6) All substances exert more or less of an absorbing effect on X-rays. In general, the absorbing effect of any given substance for a given bundle of rays depends upon the material used as a target in the tube, the nature and thickness of the absorbing substance, the history of the radiation after leaving the target, and the P. D. across the tube at the instant the given bundle of rays is given off. In general, if the target of the tube is a substance of high atomic weight, then rays from that tube will be less readily absorbed than if the target had been of low atomic weight.

When rays from an ordinary X-ray tube pass through a substance, some of the radiation is absorbed, so that the emergent beam acts more feebly on a fluorescent screen, photographic plate, selenium cell, or ionizing chamber. If rays from a platinum-target tube, operating under ordinary working conditions, are made to pass through silver, then the intensity of the emergent beam may be calculated from the formula,

$$I_2 = I_1 \epsilon^{-\lambda x}$$

in which I_1 = intensity of the incident beam.

I_2 = intensity of the emergent beam.

ϵ = base of natural logarithms = 2.7182 +.

x = thickness of the absorber.

λ = coefficient of absorption of the substance used as absorber. λ is very approximately independent of the thickness of the silver.[16]

[12] G. Schwartz, *Wein. Méd. Presse*, 1906, xlvii, 2092. *Electrotech. u. Maschinenbau*, 25, p. 452, June 9, 1907.

[13] Bordier and Galimard, *Arch. d' Elect. Med.*, May 10, 1905.
G. Holzknecht, *Arch. d' Elect. Med.*, Oct. 10, 1910.

[14] Colwell and Russ, *Arch. of Middlesex Hosp.*, xxvii, p. 63.

[15] Perreau, *Comptes Rendus*, 129, pp. 956–957, Dec. 4, 1899.
Athanasiadis, *Ann. d. Phys.*, 27, 4, pp. 890–896, Nov. 26, 1908.

[16] J. Beloit, *Arch. d'Elect. Med.*, Aug. 10, 1910.

All substances for which the above law holds true are said to be "aradiochroic." If, however, the rays are made to pass through sheets of aluminum, tin, etc., the above law does not hold. The value of λ as calculated by the formula is different for different thicknesses of the absorbing sheet, but as the thickness is increased, λ approaches more and more nearly to a constant value,[17] and the law holds approximately if the sheet is thick enough. The formula may also be made to apply approximately if the difference in thickness between two absorbing sheets is so small that the value of λ has not changed appreciably, due to the change in thickness. Absorbers which act in this way are said to be "radiochroic," and are often called "filters."

These facts may be explained by assuming that an X-ray tube sends out a complex radiation ("heterogeneous beam") having two, and sometimes three, components. For the justification of this assumption see page 302. In aradiochroic substances the coefficients of absorption for the component beams are approximately the same. In radiochroic substances the beams are unequally absorbed. If the filter is thick enough to completely absorb all but one of the components, the emergent beam is said to be "homogeneous," and the absorption law will hold accurately for any absorber through which the beam may subsequently pass, provided no secondary rays are produced. It is to be noticed that no substance is *absolutely* aradiochroic. Silver is probably the most nearly aradiochroic metal for the rays given off by a tube with a platinum or platinum-iridium target, but is quite radiochroic for the rays given off by a lead target,[18] being more opaque to the "secondary" component than to the "primary" component of the beam. If the absorber is of the same material as the target, it is more opaque to the "primary" component than to the "secondary" component. But the two absorption coefficients may be so nearly equal as to cause the absorber to appear under some conditions to be almost completely aradiochroic.[19]

If the absorber is of the same material as the target, then

---

[17] W. Seitz, *Am. d. Phys.*, 27, 2, pp. 301–310, Oct. 15, 1908.
J. Beloit, *loc. cit.*

[18] W. R. Ham, *Phys. Rev.*, xxx, 1, Jan., 1910, pp. 104–105, 118–120.

[19] G. W. C. Kaye, *Camb. Phil. Soc. Proc.*, 14, pp. 236–245, Oct. 15, 1907. *Roy. Soc. Proc. Phil. Trans. A*, 209, pp. 123–151, Nov. 19, 1908.
W. R. Ham, *Phys. Rev.*, xxx, 1, p. 112, Jan., 1910.

λ decreases as the P. D. across the tube is raised, and the decrease of λ with the increase of P. D. is much more marked the higher the P. D. employed.[20]

If the absorber is a chemical compound, the total absorption under any specified conditions is the sum of the various absorptions caused under those conditions by the various atoms and radicals of which the absorber is composed.[21]

(7) When X-rays are directed toward a given layer of flesh, in general, some of them pass through, while others are absorbed and give up their energy to the flesh. If sufficient energy is thus delivered to the flesh, serious pathological changes result which are of great importance from the view-point of the physician, but which do not concern the physical investigator, aside from the question of his own self-protection. A person in good health may have several radiographs taken (sufficient for ordinary diagnostic work) by a well-informed operator, without any danger of an X-ray burn, but the operator, or research-physicist, must, because of the possibility of long-continued exposure, or more often because of frequent repetition of short exposures, protect himself most carefully. The German Röntgen Society [22] recommends that the protection consist of at least two millimetres of sheet lead, eight millimetres of X-ray proof rubber impregnated with lead, or lead glass from ten to twenty millimetres thick.

(8) Besides exhibiting the above-mentioned characteristic properties, X-rays also show properties which have caused them to be classed as a form of wave motion. When a narrow beam of X-rays is passed through a crystal parallel to a cleavage plane the emergent beam is broken up into a number of smaller beams symmetrically placed so that the effect as shown on a photographic plate, gives the appearance of a diffraction pattern.[23]

Stark[24] contends that this is not a true diffraction pattern,

---

[20] W. R. Ham, *Phys. Rev.*, xxx, 1, pp. 108, 111–113, Jan., 1910.

[21] W. Seitz, *Phys. Zeitschr.*, 13, pp. 476–480, June 1, 1912.
Blennard and Labesse, *Comptes Rendus*, 1896, cxxii, pp. 723–725.

[22] *Archives of the Röntgen Ray*, July, 1913.

[23] W. Friedrich, P. Knipping, M. Laue, *K. Bayer. Akad. München. Ber.*, pp. 302–322, 1912. *Le Radium*, 10, pp. 47–57, Feb., 1913.
M. de Broglie, *Comptes Rendus*, 156, pp. 1011–1012, March 31, 1913.
T. Terada, *Nature*, 91, pp. 125–126, April 10, 1913; p. 213, May 1, 1913.

[24] *Phys. Zeitschr.*, 13, pp. 973–977, Oct. 15, 1912.

but most writers assume that the evidence points toward a true diffraction, and the theoretical basis of such an assumption is given by M. Laue, W. L. Bragg, and G. Wulff.[25]

The results of Friedrich and Knipping's experiments point to a wave length for X-rays of the order of 10^{-9} cm. This is of the same order as the value given by Plank's theory and as the value found by Walter and Pohl.[26]

When a pencil of X-rays is allowed to impinge on the cleavage face of a crystal at grazing incidence, a portion of the beam is reflected and the angle of reflection is equal to the angle of incidence.[27] Since this reflection is from the molecules of the cleavage face, the effect corresponds to that obtained when light is allowed to fall on a reflection diffraction grating, and there appears not only the truly reflected beam, but also a series of interference bands.[28]

Experiments with magnetic fields show that no measurable deflection is produced even by a magnetic field of 19,000 gauss. No experiments on the velocities of X-rays have been conclusive.

PRIMARY X-RAYS.

If negatively-charged particles of matter (variously called corpuscles, β particles, kathode rays, and electrons) are shot out at high velocities toward a target, they will experience a great decrease in velocity upon entering the face of the target, and during the time that this decrease in velocity occurs, X-rays are produced. Such rays are called "primary rays." Although the point has not been as yet definitely settled, their properties

[25] W. Friedrich, P. Knipping, M. Laue, *loc. cit.*
W. L. Bragg, *Camb. Phil. Soc. Proc.*, 17, 1, pp. 43–57, Feb. 14, 1913.
G. Wulff, *Phys. Zeitschr.*, 14, pp. 217–220, March 15, 1913.

[26] Walter and Pohl, *Ann. d. Phys.*, 29, 2, pp. 331–354, May 21, 1909.

[27] W. L. Bragg, *Nature*, 90, p. 410, Dec. 12, 1912.
C. G. Barkla and G. H. Martyn, *Nature*, 90, p. 435, Dec. 19, 1912.

[28] C. G. Barkla and G. H. Martyn, *Nature*, 90, p. 647, Feb. 13, 1913. *Phys. Soc. Proc.*, 25, pp. 206–214, April 15, 1913.
E. Hupka and W. Steinhaus, *Deutch. Phys. Gesell. Ver.*, 15, 5, pp. 162–163, March 15, 1913.
H. B. Keene, *Nature*, 91, p. 111, April 3, 1913.
E. A. Owen and G. G. Blake, *Nature*, 91, p. 135, April 10, 1913.
H. S. Allen, *Nature*, 91, p. 268, May 15, 1913.
E. Hupka, *Nature*, 91, p. 267, May 15, 1913.

seem to depend only upon the rate of retardation which the charged particles experience at the target, and this, in turn, depends very approximately upon the square root of the P. D. across the tube, upon the pressure of the gas in the tube, and upon the atomic weight of the target.

When the kathode rays strike the target, they are not stopped instantaneously at the surface, but merely suffer retardation, so that they penetrate for some distance into the body of the target. After once entering the target, the particles no longer all move in the same general direction, but travel more or less radially. If, for a given velocity of kathode rays, we imagine the target to be made thicker and thicker, a thickness will be reached at last for which there are as many particles emerging in one direction as in any other. This thickness is called "The depth of complete scattering." [29] In aluminum it is .015 cm.; in copper, .001+ cm.; in silver, .001+ cm.; in gold, .00020 cm.; in lead, .00025+ cm. at 90,000 volts. It varies directly as the voltage employed across the tube.

Those primary rays which are able to overcome the absorbing effect of the target reach the surface and emerge into the vacuum space of the tube. Measurements have shown [30] that if the P. D. across the tube is made very small, then the primary rays, at the moment of generation, have their maximum of intensity in a direction perpendicular to the kathode stream, and a minimum of intensity in a direction parallel to the kathode stream. This effect is called "polarization." As the P. D. across the tube is increased, the polarization is decreased, until finally it becomes immeasurable. This is explained by assuming that at the higher potentials the rays formed by the initial retardation of the kathode

[29] J. A. Crowther, *Roy. Soc. Proc.*, 80 A, pp. 186–206, March 5, 1908.
W. R. Ham, *Phys. Rev.*, xxx, 1, pp. 119–121, Jan., 1910.

[30] R. Blondlot, *Comptes Rendus*, 136, pp. 284–286, Feb. 2, 1903. *Nature*, 69, p. 463, March 17, 1904.
C. G. Barkla, *Roy Soc. Phil. Trans.*, 204, pp. 467–479, May 31, 1905. *Roy. Soc. Proc.*, 74, pp. 474–475, March 16, 1905.
H. Haga, *Konik. Akad. Wetensch. Amsterdam Versl.*, 15, pp. 64–68, July 20, 1906.
J. Herwig, *Ann. d. Phys.*, 29, 2, pp. 398–400, May 21, 1909.
E. Basseler, *Ann. d. Phys.*, 28, 4, pp. 808–884, March 16, 1909.
L. Vegard, *Roy. Soc. Proc.*, Ser. A, 83, pp. 379–393, March 22, 1910.
W. R. Ham, *Phys. Rev.*, xxx, pp. 96–121, Jan., 1910.
F. C. Miller, FRANKLIN INST. JOUR., 171, pp. 457–461, May, 1911.

stream are negligible in their effects when compared with those rays which come out in all directions from the depth of complete scattering.

SECONDARY RAYS.

When X-rays of sufficient penetrating ability are made to impinge upon a substance, that substance itself becomes a source of X-rays, which are called "secondary rays," and in general these secondary rays have penetrating abilities widely different from the exciting or "primary" rays, and the penetrating ability depends upon the substance used as a radiator.[31]

Radiators may be divided in the order of their atomic weights into four groups, as shown below. The radiations given out by the members of each group are very much alike.

Group 1 (1–32).—H–S. When excited by a beam from a "soft" tube the members of this group give off little, if any, real secondary radiation, but rather a scattered (one might almost say "diffusely reflected") radiation which is of the same nature as the exciting beam, and which is polarized in a plane perpendicular to the direction of the parent kathode stream. If the tube is made moderately "hard" (*i.e.*, if it gives off moderately penetrating rays), then a slight amount of true secondary radiation shows itself, and if the tube is very "hard," a well-defined secondary beam is given off having a penetrating ability much different from that of the exciting rays.

Group 2 (52–65).—Cr–Zn. This group gives off a beam composed almost entirely of a true homogeneous secondary radiation even when excited by rays from a "soft" tube, but this radiation has little penetrating ability. With a given excitation, the ionization produced by it is almost 100 times that produced by an equal mass belonging to group 1.

Group 3 (107–125).—Ag–I. If the exciting beam is only of moderate penetrating ability, this group gives off mostly a scattered radiation, but, unlike that from group 1, it is unpolarized, and there is a noticeable amount of true secondary radiation present. The relative amounts of scattered and secondary radiation vary greatly with small changes in the character of the exciting rays.

[31] C. J. Barkla and C. A. Sadler, *Nature*, 77, pp. 343–344, Feb. 13, 1908. *Nature*, 80, p. 37, March 11, 1909.

Group 4 (183–206).—W–Bi. These substances resemble group 2 in their action. For all the above elements the penetrating ability of the true secondary rays is independent of the intensity or of the penetrating ability of the exciting beam, but is a periodic function of the atomic weights of the radiating elements.[32]

If the radiator is a chemical compound, the component atoms and radicals determine the character of the secondary rays produced.[33]

The rays coming from salts are composed of (1) a homogeneous radiation having the same penetrating ability as that from the metal itself, and (2) a scattered primary radiation considerably more penetrating than (1) due to the acid radical. If a metal occurs in the acid radical it has no individual effect, but merely acts along with the rest of the radical.[34]

Barkla and Sadler [35] have shown that if the incident primary rays are less penetrating than are the secondary rays which are characteristic of the radiator used, then no secondary rays are produced, but if the incident primary rays are more penetrating than the characteristic secondary radiation, then secondary rays are produced.

The production of secondary X-rays is very analogous to the production of fluorescent light. In fact, the analogy is so close that some writers are adopting the term "Fluorescence Röntgen radiation." If the penetrating ability of the exciting primary rays is increased beyond that necessary to first excite secondary radiation, it is often possible to obtain from the same radiator still another group of secondary rays having a different penetrating ability than the first, but this second group seems always to be identical with the first group from some other radiating substance.[36]

Chapman and Piper [37] tried to detect a continuance of secondary radiation after excitation from the primary rays had ceased, but were unable to detect even 1/250 of the original

[32] C. G. Barkla and C. A. Sadler, *Phil. Mag.*, 16, pp. 550–584, Oct., 1908.
[33] J. A. Crowther, *Phil. Mag.*, 14, pp. 653–675, Nov., 1907.
[34] J. L. Glasson, *Camb. Phil. Soc.*, pp. 437–441, June 14, 1910.
[35] Barkla and Sadler, *Nature*, 80, p. 37, March 11, 1909.
[36] R. Whiddington, *Nature*, 88, p. 143, Nov. 30, 1911.
J. C. Chapman, *Roy. Soc. Proc.*, Ser. A, 86, pp. 439–451, May 8, 1912.
[37] Chapman and Piper, *Phil. Mag.*, 19, pp. 897–903, June, 1910.

radiation 1/3000 second after the exciting primary rays were removed.

It was stated on page 299 that the primary rays from the target of an X-ray tube must pass through a thickness of the target before they can emerge. It would be expected that such rays would excite that secondary radiation which is characteristic of the substance used as a target. There is also some evidence to show that the kathode stream itself may cause the target to give off its characteristic radiation if the velocity of the kathode stream is large enough.[38]

Ham[39] has been able, by the use of proper absorbers, to filter out the secondary rays coming from his tube, leaving only the primary rays. He found that the ratio of the secondary radiation to the primary was increased by an increase in the P. D. across the tube. The rays coming from an ordinary X-ray tube are, therefore, heterogeneous, and since the P. D. necessary to cause a discharge to pass through the tube varies with the condition of the tube this heterogeneity is constantly changing.

On account of the wide variation in the character of the rays from tubes with the P. D. and current employed from instant to instant, it is essential that practically all experimental data concerning the action of X-ray tubes or of the rays themselves be accompanied by a statement showing:

(1) The P. D. employed and its wave form. If the maximum P. D. is measured by a spark-gap, the exact shape and dimensions of the terminals of the gap should be given. If the P. D. is measured by some other means, complete description should be given. If the wave form is not known, *complete* description should be given of the means used to obtain the exciting current.

(2) The number of milliampères used and the kind of milliammeter used (that is, E. M., hot-wire, etc.). If the tube is of the Lilienfeld type,[40] the size of the regulating current must also be given.

(3) Exact description of the tube, including maker's name, serial number (if any), classification given by maker, dimensions, material used as target, hardness of tube at time of experiment,

[38] R. T. Beatty, *Roy. Soc. Proc.*, Ser. A, 87, pp. 511–518, Dec. 13, 1912.
[39] W. R. Ham, *loc. cit.*
[40] *Fortsch. a. d. Gebiete d. Röntgenstrahlen*, vol. 20, No. 5, 1913, p. 448.

and condition of tube (*i.e.*, "grows harder with use," "hardness nearly constant," or "grows softer with use").

(4) Number of seconds the tube is used for one "run." Much of the published data to date is useless because of the failure to record one or more of the items mentioned above, since without such information the results can neither be interpreted properly nor exactly duplicated by any other experimenter.

MEASUREMENT OF QUALITY, QUANTITY, AND INTENSITY.

The penetrating ability of an X-ray beam is called its "quality." It is usually arbitrarily measured by the thickness of aluminum which will permit the same intensity of radiation to pass through it as passes through a standard thickness of silver. Equality of intensity is determined either by means of the illumination of a fluorescent screen or by the blackening of a photographic plate. There is no experimental evidence that measurements of the same beam made in the two ways will agree, but it may be possible that some fluorescent screen may be found which will have the same effect as some particular photographic plate.

There are several methods in use for measuring the quantity of radiation passing a given point in a given time. Among these are:

(1) Precipitation of iodine from its solution in chloroform.

(2) Precipitation of calomel from a mixture of ammonium oxalate and bichloride of mercury.

(3) Change in color of barium platino-cyanide.

(4) Total ionization produced in air by the rays.

(5) Density of blackening of a photographic plate.

(6) Heating of a bolometer.

(7) Change in resistance of a selenium cell.

(8) The quantity of radiation is taken as proportional to the product of the P. D. across the tube, the current through the tube, and the time.

The first method has the objection that X-rays are not the only means of causing the precipitation. In method 2 a fresh solution must be employed for each reading. In spite of the fact that method 3 is open to the same objection as method 1, it has

met with some favor, and there are numerous types of dosage-meters based on this principle, each with its own scale of tints. Tables have been published (for instance, in *Arch. d'Elect. Med. du Bordeau*, July, 1910) by which readings taken on any of the arbitrary scales of the above three methods may be converted into the reading on any of the other arbitrary scales, but the scales in method 3 are only accurate for rays within some definite range of hardness. These three methods have the great advantage that they record instantaneously the quantity of radiation absorbed by the instrument, and may, therefore, be used as dosage-meters. Method 4, although it may be made very exact and although it is excellent from the point of view of the physicist, is unsuited to the requirements of the physician, in that it can not be well used in the summer. It has not been checked against the other methods. If the hardness of the tube and the kind of plates and method of their development are specified, method 5 is useful in cases where it is not necessary to shut off the tube as soon as a certain quantity of radiation has been given off. Methods 6 and 7 have not as yet found much favor. They have not been checked against the other methods. Method 8 is entirely empirical for each apparatus, and a change in any part of the outfit necessitates a new calibration. Although a given operator may use this method with his particular outfit, he cannot easily compare his data with that of another operator having an outfit which differs from his own in any respect.

Intensity has been measured in three ways:

(1) Variation of distance from the tube (all other conditions being unchanged).

(2) Brightness of a fluorescent screen.

(3) Quantity per second (measured by any method given in the previous paragraph).

Method 2 can not be used to compare heterogeneous beams of different compositions (see page 293), and as a result is not accurate when used to compare the rays given off by a tube at one time with the rays given off by the same tube at another time under even slightly different conditions. Method 3 is open to the advantages or disadvantages of the particular method employed to measure quantity.

ON THE THEORETICAL EFFICIENCY OF THE LINDE PROCESS OF LIQUEFYING AIR.*

BY

M. M. GARVER, B.S.,

Associate Professor of Physics, Pennsylvania State College.

NOTWITHSTANDING the voluminous literature on the subject of the liquefaction of air, I fail to find what seems to me a really satisfactory exposition of its theoretical features based on fundamental thermodynamic facts and laws. Some important theoretical points are either unnoticed or only incidentally touched on,—*e.g.*, the fundamental influence of molecular attractions on the possibility of liquefaction at all; and, more particularly, the peculiar rôle molecular attractions play in a continuous isothermal process, where all the heat abstracted from the compressed air is confined to what is given out at readily available temperatures such as is afforded by the ordinary water supply. For instance, in Poynting and Thomson's Heat,[1] the authors of which may be regarded as occupying positions of the highest authority on any subject to which they give their attention, the cooling in such process is merely incidentally attributed to the work done in overcoming molecular attractions; and the reasons for the statement are given only by calling attention to an apparent analogy of the process to that of the porous plug experiment. From this fact I conclude that probably no more satisfactory, concise, and non-mathematical explanation was known to them or it would have been given, or at least referred to. A more complete theoretical explanation *may* have been published, but, if so, I also am unacquainted with it. I know of no more satisfactory, concise explanation of the theory than they offer; but, in my judgment, their exposition is too brief and incomplete to enable one to comprehend the process as a whole. Other writers, again, attribute the cooling to work done on the gas by itself. While this statement is true, in a sense, it may be misleading, because in the continuous process work is continually

* Communicated by the author.

[1] 3rd ed. (1908).

done *on* the gas as well as *by* the gas; and part of the work done by the gas goes to heat it. The part of the work which does not produce heat consumes heat and produces the cooling. In general, the theory seems to be derived from the workings of the apparatus rather than the converse of designing an apparatus to fulfil certain theoretical conditions.

The difficulties met with in trying to form a clear judgment, based on fundamental thermodynamic conceptions, of the regenerative process as applied to the liquefaction of air, and of the relation of this process to the porous plug experiment, lead me to think that the theoretical results at which I have arrived may be of general interest.

All the early attempts at the liquefaction of gases were made with a definite quantity of gas, and the result, when successful, could in many cases be attributed to the doing of *external* mechanical work by the gas after it had been sufficiently compressed and cooled. Hence the impression is apt to linger in the mind that by some process,—by some mechanical appliance,—the air in the continuous process should be made to do external mechanical work during expansion in order that it may be cooled thereby and a larger output of liquid obtained. In fact, one of our best text-books on general physics makes the definite statement that if the compressed air were expanded against a moving piston so as to do mechanical work a larger supply of liquid air might be obtained. Another standard work represents the expanded and cooled air as passing a *second time* through the pump and cooler, so that the operation may be repeated and the effects accumulated. Now it seems to me that if the correct theory were known and published such statements would not be made, for they are not in accordance with thermodynamic theory. But without some guiding theoretical principle one is apt to be overimpressed when comparing the 24 calories of the litre-atmosphere unit of work with the slight cooling effect, of about one-fourth of a degree centigrade per atmosphere in the expansion of air noticed by Joule and Thomson in their celebrated porous plug experiment. Yet it may be shown from general principles, without reference to special apparatus, that this slight cooling effect, in so far as it represents internal molecular work in the form of a displacement against a resistance (molecular attractions), is the sole source of the cooling during an "isothermal" continuous

process. The "isothermal" case is the general case and is theoretically the most interesting. Of course, special refrigerants may enable us to liquefy a larger percentage of the compressed air; but the two processes, considered as one, will be less efficient than the simple isothermal process, as may be seen in the sequel.

It is not the present purpose to discuss the general theory of refrigerating processes further than necessary to show in a general way the difference between a continuous process leading to the liquefaction of a portion of the gas operated on and one adapted to the production of a moderate cooling of a large mass of material. In the latter case both external and internal work may be utilized; in the former only "internal" work. A correct theory of the continuous liquefying process will disclose the scientific reasons for the difference in practice in the two cases of refrigeration and liquefaction, and will aid in designing the apparatus for a given purpose. The experimental basis of the theory of liquefaction by a continuous process is the famous porous plug experiment, while the continuous refrigerating process utilizes the heat of vaporization of a volatile liquid. In the cooling and ventilating process the cooling is mainly due to the external work done by the expanding air.

THE POROUS PLUG EXPERIMENT—PRELIMINARY CONSIDERATIONS.

In the usual discussion of a gas, escaping into a vacuum, no details are given, but merely the simple conclusion, confirmed by experiment, that because no external work is done the energy, and consequently the temperature, remain unchanged. But evidently the introduction of the first increment of gas into a vacuum produces a pressure, and each successive increment meets the pressure caused by the earlier portion. Since the gas is indefinitely expansive, we may regard each increment as filling the whole space, or volume; hence the work is simply $v\int_0^p dp = pv$. But this is equal to the kinetic energy of the gas, so that in this case all the work done while forcing in the later portions of the gas against the existing pressure is transformed into the kinetic energy pv. If no change of temperature occurs, we may say that, in this case, the work done *by* the gas is equal to the work done *on* it.

In the general case of a fluid, compressible or incompressible, the external work required to transfer the mass m from a region of steady pressure p_1 to another region of steady pressure p_2 will be equal to $m\left(\frac{p_2}{\rho^2}-\frac{p_1}{\rho_1}\right)$, the subscripts representing the two states respectively. For since each pressure is constant the work done *by* region *one* must be equal to p_1v_1, and the work done *on*, or *in*, the region *two* must be equal to p_2v_2. The difference, whether positive or negative, represents the external work done and supplied from outside. Since $m=\rho v$, where ρ is the density and v is volume of the mass m, we may write $\frac{m}{\rho}$ for v, or

$$w_2-w_1=w=m\left(\frac{p_2}{\rho_2}-\frac{p_1}{\rho_1}\right).$$

We may note three cases: *First*, when there is no change in density, or the fluid is an incompressible liquid, and $w=\frac{m}{\rho}(p_2-p_1)$. *Second*, when the density is strictly proportional to the pressure, in which case the parenthesis $\left(\frac{p_2}{\rho_2}-\frac{p_1}{\rho_1}\right)=0$ and no work is done, or, $p_2v_2=p_1v_1$. In the *third* case, however, the external pressure may be diminished by internal attractions depending upon the distance apart of the molecules, so that when $v_1<v_2$ then $p_1v_1<p_2v_2$, when the temperatures are equal, or the external work done *on* the gas is no longer equal to the external work done *by* the gas, because a part of the energy is used during expansion in doing *internal* work in separating the molecules.

In the text-books and in the various discussions of the porous plug experiment much attention is given to the work done on and by the gas. But by considering only "steady" states and a constant stream with "steady" pressures and temperatures, with no energy in any form entering or leaving the stream at any point, the case in nowise differs from the transmission of energy in the direction of its length by a rod whose state of strain is steady, when it is perfectly evident that the rod transmits without loss what is impressed on it, both as to force and displacement. The same is true of a belt whose state of strain is steady, except that a "pull" replaces the "push." Likewise, when the temperature and pressure of a gas, in a given volume of gas, are kept constant while additional gas is being forced in, the stress

introduced by the entering gas must be relieved at some point by the escape of an *equal* amount, or the temperature and pressure would be changed. The work done *by* the escaping portion must, *by* the law of conservation, be equal to the work done *on* the gas if the state of the gas is *steady*, just as in the cases of the rod and the belt.

THEORY OF THE POROUS PLUG EXPERIMENT.

Consider an enclosed space, or chamber, A, into which gas is being forced by a continuous steady pressure, isothermally (that is, through a cooling device which keeps the temperature constant). Now suppose that when the pressure in A has reached a certain value the gas escapes into another and larger chamber, B, through a constant pressure valve, or other device, as in the porous plug experiment, and that likewise the gas escapes from B at a pressure much lower than that at which it escapes from A into B. (The pressure in B may be the atmospheric pressure.) Now if no heat or other form of energy enters or leaves the compartments *except as carried by the gas* from A into B, we shall, after a time, have a "*steady state*" throughout the whole system. Whatever the temperatures and pressures in the two compartments may be, after the state becomes steady, *the energy per unit mass of the gas must be the same in both A and B.* We need make no assumptions as to the applicability of Boyle's law, for the same stream, and therefore the same mass of substance and the same quantity of energy, are passing through both at the same rate; and in both compartments both are receiving the same quantity and both are giving out the same quantity without changing the steady temperature and pressure. Since the volume of each chamber is constant, any change in the total energy in either A or B implies a corresponding change in the temperature, pressure, volume, or density; but these are assumed to be steady, or unchanging. Therefore, if we represent the total energy per unit mass by E, then $E_1 = E_2$, where the subscripts represent the compartments A and B respectively. But, since the energy in each case may consist of kinetic and potential energies in different proportions, we may write $E_1 = k_1 + w_1$, and $E_2 = k_2 + w_2$, or $k_1 + w_1 = k_2 + w_2$, where k represents kinetic and w the potential energies.

Experiment shows that the specific heat of a gas is nearly

independent of temperature and pressure, provided it is so determined as to be independent of the work done on or by the gas during the necessary change of temperature. Therefore, if the heat of a gas is proportional to the kinetic energy of the gas, we may write

$$\frac{H_2}{H_1} = \frac{T_2}{T_1} = \frac{k_2}{k_1}$$

where T represents the absolute temperature. These ratios may also be written

$$\frac{T_1 - T_2}{T_1} = \frac{k_1 - k_2}{k_1} = \frac{w_2 - w_1}{k_1}$$

since $k_1 - k_2 = w_2 - w_1$.

In the case of atmospheric air, Joule and Thomson's experiment showed that $T_2 < T_1$, hence that $w_1 < w_2$, or the potential energy diminishes with the volume. Amagat's experiments on the isothermal compression of air show that pv decreases with the volume for values of p less than 75 atmospheres. From these two experimental results we may conclude that the internal attractions aid appreciably in diminishing the external pressure p in the case of air.

Let us now examine the influence of this molecular attraction during the isothermal compression and subsequent expansion, during which the gas does internal work on itself, and the escaping portion is reheated, notwithstanding the internal work it does in overcoming molecular attraction during the expansion.

When an amount of external work W is done on a gas, compressing it isothermally, the internal attractions, if they exist, will supply a quantity of internal work w which will also be abstracted as heat. The total will be $W + w = H_1$ (say), the total heat taken from the gas during isothermal compression. Now since the heat equivalent of the total work, $W + w$, has all been taken away, the total energy per unit mass of the gas has been diminished by the amount w. Hence, if the gas by any process whatsoever be allowed to expand without receiving energy in some form from outside sources, the internal work w will have to be done; and the heat equivalent of that work, if obtainable from no other source, will be taken from the kinetic energy of the gas itself, with a resulting fall in temperature. If w represents the heat abstracted from *one* gramme of the gas, producing a temperature drop, t, in the whole mass, then if taken from one-half

of the gas the temperature drop will be $2t$; and if taken from the n^{th} part, nt degrees, if the specific heat is uniform. Hence it is plain that if this temperature difference can be maintained in such manner that the warm, compressed air can be made to warm the cooler expanded air so as to return it to the atmosphere at its original temperature and pressure, a portion of the substance, for lack of energy, must perforce, remain behind in the apparatus. Let us, therefore, introduce a slight, but important modification in the arrangements of the two compartments, A and B, described above, keeping the other features unchanged. Suppose the compartment A to consist of a long copper tube, or other good conductor of heat, and that B is a concentric non-conducting tube, so that it is free to receive heat from A but none from outside sources. At the beginning of the process an abrupt, or sudden, change of temperature will occur at the point where the pressure changes. Since the expanded air is always cooler than the compressed from which it issues, and the two are separated only by a thin conducting partition, the compartment A will *at first* give out energy *faster* than it receives it; but this state of affairs can not continue indefinitely. It will cease and become "steady" when the heat of liquefaction occurring in A will limit its output to its intake. If perfect heat insulation were possible, the condition of maximum efficiency would require that the escaping air be restored to the atmosphere at its original temperature and pressure. For, if the air leaves the apparatus at any lower temperature than this, all the heat that might have been abstracted has not been carried away, hence the possible amount of liquid would be diminished.

It has been shown that if the w units of heat abstracted from one gramme, and causing a drop of t degrees, could be concentrated on the one-n^{th} part of the mass it should cause a drop of nt degrees. Assuming that the specific heat is uniform and constant and independent of the volume, we may make an estimate of the quantity of liquid obtainable with a given compression. From Amagat's, and other experiments the product pv for air is a minimum at about 75 atmospheres, and does not exceed normal values for pressures less than 150 atmospheres. Let us take 160 atmospheres for convenience. We may take the specific heat at constant volume as .177. The heat of vaporization is given as 50 calories per gramme. Hence, to lower the temperature of a gramme of air from 20° C. to −190° C., or 210°, will supply 210

×.177 calories,—*i.e.*, 37 calories. Hence, to cool and liquefy one gramme under the given conditions would yield 87 calories. According to the Joule and Thomson experiment, the cooling is ¼ degree per atmosphere, or 40° C. for 160 atmospheres, indicating 7 calories per gramme. But since 87 calories must be abstracted, under the given conditions, then, if the apparatus is perfect, between 1/12 and 1/13 of the whole mass should be liquefied.

The question still remains: Could not a larger output be obtained by making the compressed air do external work while expanding against a moving piston?

Theoretically, the maximum effect can be produced only when the process is reversible. The maximum amount of work, and hence the production of the maximum drop in temperature, requires that the expansion be adiabatic; but the data are not very reliable over such a wide range of temperature and pressure. The formulas apply only to gases, but as a substance approaches liquefaction it becomes properly a vapor and the formulas mere approximations. If, however, we apply the formula $\int_1^2 pdv$ to the adiabatic expansion of air from 160 atmospheres to 1 atmosphere, we get from

$$\int pdv = -\frac{v_0 p_0^{\frac{1}{k}}}{k} \int_1^{160} \frac{dp}{p^{\frac{1}{k}}} = 303.5$$

litre atmospheres, or 7275 calories from 200 grammes of air (one litre at 160 atmospheres) at 20° C. This is less than 37 calories per gramme, the amount required to lower the temperature to the boiling-point, or liquefying temperature at atmospheric pressure, without producing any liquefaction. Practically the same result is obtained by applying the formulas for adiabatic expansion and temperature change for a pressure change from 160 atmospheres at 20° C. to 1 atmosphere at T degrees absolute. The resulting temperature is found to be 67° absolute, which is only 10° below the normal boiling-point of nitrogen. This gives only about 1.8 calories per gramme toward liquefaction, which requires 50 calories per gramme. The two results agree as well as could be expected, in consequence of the uncertainty in the value of the specific heat used, 0.177. The value of k used was 1.41.

In any case, perfect heat insulation and perfectly reversible adiabatic expansion would be required to obtain *any* liquid at all by the doing of external work, if the compression does not exceed 160 atmospheres at 20° C. Of course, if the pressure were reduced below one atmosphere, a larger change in temperature could be produced. But such procedure would require the application of work from the outside and would cut down the efficiency. Since air costs nothing to procure, the maximum efficiency is reached when the ratio, $\frac{\text{Liquid obtained}}{\text{Work done}}$, is a maximum.

The reason of it becomes plain when we reflect that *combined* pressure and low temperature are the important elements in the liquefaction of a gas. By the expansion while doing work one important element, the compression, is nullified. It is impossible to do work and retain the compression.

It was shown in a preceding paragraph that, from the temperature relations, ideal conditions should permit of about 1/13 of the air being liquefied with 160 atmospheres compression at 20° C. It may be of interest to express this relation in terms of the work done by the interior molecular attractions.

Since the rejected air is assumed to have the same temperature and pressure as the original, the ratio of the energies will be the same as the ratio of the masses. Let M_1 represent the initial mass and M_2 the rejected mass, H_1 and H_2 the heat equivalents of the work W and w, respectively, where W represents the external work done during isothermal compression and w the internal work of molecular attraction. Then we must have

$$\frac{M_1}{M_2} = \frac{H_1+H_2}{H_1} = \frac{W+w}{W} \text{ or, } \frac{M_1-M_2}{M_2} = \frac{w}{W} = \frac{L}{M_2}$$

where L represents the mass of the liquid. Or, the ratio of the liquid mass to the mass of the rejected air is in the same proportion as the work due to the molecular attractions is to the external work done during isothermal compression. We may test this relation, using the same data as for adiabatic expansion,—*i.e.*, 160 atmospheres and 20° C.

We found previously that the experimental value of ¼° per atmosphere indicates 7 calories per gramme internal work. For 200 grammes (as before) the value of $w = 1400$ calories. Now, to compress 200 grammes *isothermally* would require 818 litre

atmospheres of work, or 19,600 calories. This is exactly 14 times 1400, or, the ratio $w/W = 1/14$. This, under the circumstances, may be regarded as a very fair agreement. At all events, molecular attractions are not a vanishingly small quantity if they do 1/14 of the work during isothermal compression, and correspondingly oppose adiabatic expansion.

STATE COLLEGE, PA., December 30, 1913.

The Bleaching Action of Hypochlorite Solutions. S. H. HIGGINS. (*Chem. Soc. Proc.*, xxix, 302.)—Bleaching powder solution to which an excess of boric acid has been added has very energetic bleaching properties, because the boric acid merely liberates hypochlorous acid from the hypochlorite, whereas an excess of hydrochloric acid produces free chlorine and a solution of very weak bleaching properties. If, however, calcium carbonate be added to the latter solution, hypochlorous acid is regenerated, and the bleaching properties are restored. The addition of hydroxides to hypochlorite solutions opposes the hydrolysis of the hypochlorite, and retards the bleaching action, whereas the addition of small quantities of acids assists the hydrolysis and stimulates the bleaching action; the effect on the bleaching properties of the solution is due to the active mass of the free hypochlorous acid present, but in the one case reduced and in the other augmented. Even in the presence of a large excess of hydroxides the solutions have little bleaching effect, which is probably due to a small amount of hypochlorous acid being still present in solution in spite of the opposition of the hydroxide to the hydrolysis of the metallic hypochlorite. All the experiments point to the conclusion that hypochlorite solutions owe their bleaching properties to the free hypochlorous acid present in solution. Sometimes there is a secondary reaction between the hypochlorous acid and any neutral chloride present, producing nascent chlorine of energetic bleaching properties, but the main action is one of direct oxidation by the hypochlorous acid. If chlorides are produced, their stimulating effect on the bleaching action is negligible.

Conductivity of Copper. ANON. (*Brass World*, x, 1, 10.)—The electrical conductivity of copper depends on the total amount of impurities and not upon any one element. This is why the conductivity test is so valuable in determining the purity of copper. The total of all the impurities is shown, and thus the purity of the copper is indicated. Amounts of impurities that will defy detection by chemical analysis are found when the electrical conductivity test is applied. It is, therefore, one of the most valuable tests known to metallurgy.

HIGH PRESSURES AND FIVE KINDS OF ICE.*

BY

P. W. BRIDGMAN, Ph.D.,

Jefferson Physical Laboratory, Harvard University.

THE experiments which I am about to describe are experiments in the field of very high pressures, which is a practically new field. Under conditions of high pressure, many of the ordinary properties of matter are changed; and the bursting strength of vessels in which such pressures are produced is found to bear no relation to their strength under ordinary conditions. In conducting the following investigations on the effect of very high pressures on water, it was found necessary to make many preliminary experiments on the strength of the containing vessels before accurate measurements of pressure could be made. In the course of this preliminary work many interesting facts concerning the behavior of materials under high pressures were disclosed. In this paper will be given, firstly, some of the results of the preliminary experiments on the strength of the containers, and then a description of the experiments made to ascertain the effect of high pressures on water. The paper will be, in large part, a record of my own experimental work.

By way of introduction, it is perhaps desirable to give some idea of the magnitude of the pressures involved. The highest pressures which are ordinarily familiar to us are probably those of modern high-power artillery; the average firing pressure exerted in many of our large guns is about 2000 atmospheres, or 30,000 pounds per square inch. The highest pressures reached in the experiments which I am about to describe are ten times this amount; that is, 20,000 atmospheres, or 300,000 pounds per square inch. A pressure of 20,000 atmospheres, if exerted against a rod of steel one inch square, would enable it to support a locomotive weighing 150 tons. The highest pressure I know of that has been previously measured is 10,000 atmospheres; this was produced by the explosion of nitroglycerin in a closed vessel; it is about one-half the pressure recorded in the present experiments.

* Abstract of paper presented at the meeting of the Section of Physics and Chemistry held Thursday, November 13, 1913.

Nitroglycerin subjected to the pressures attained in the following experiments would lose all ability to explode. The pressure exerted at the bottom of the ocean at, say, a depth of six miles is about 1000 atmospheres; a pressure of 20,000 atmospheres would, therefore, be exerted at the bottom of an ocean 120 miles deep. If the average density of the rocks of the earth's crust is taken as 2.5, 20,000 atmospheres is the pressure which prevails at a depth of fifty miles below the surface of the earth.

It should be borne in mind that in all the experiments made the pressures were produced in a liquid, which must be held in a container. It is a comparatively simple matter to produce pressures as high as 300,000 pounds per square inch in a solid piece of steel, but it is another matter to maintain such a pressure in a liquid and prevent all leaking of the latter from the container.

The most essential part of the preliminary work was to design a packing that would keep the vessel in which the pressures were to be produced absolutely tight, and prevent the liquid from leaking from it. The feature of the form of packing finally designed is that it is made tighter and tighter by the pressure in the vessel itself; the greater the pressure obtaining in the vessel, the less can the liquid leak. Most of the packing in ordinary use is made tight by compressing it by means of a screw; a packing so compressed will leak as soon as a pressure is exerted on the liquid it holds back equal to that initially produced on it by the screw; further, the pressures that are here dealt with are much greater than any pressures it is possible to produce by such means. The ordinary screw-tightened packing is, therefore, always certain to leak. With a packing that tightens itself by the pressure in the vessel, however, the only limit to the pressures that can be reached is set by the strength of the vessel itself.

The second part of the preliminary work consisted in finding what limits of pressure a steel vessel will support, steel being selected as the best material of which to make the container. In all the experiments the pressures were produced by pushing a piston, by means of a hydraulic press, into the cylinder containing the liquid, and this means of producing the pressure immediately introduces two essentially different problems. The first is the consideration of the strength of the steel piston, and the second that of the strength of the steel cylinder. These problems are independent, as these two parts of the apparatus

are subjected to different strain. In the piston the strain is one of compression, while in the cylinder it is one of bursting, or tension.

It was found by experiment that the best material for the piston was glass-hard steel. A steel that is left glass-hard is usually too brittle to use, and its temper has to be drawn, but this process makes the steel a little softer, so that it will not support so high a compression as when left glass-hard. Under the conditions in the experiments the piston was subjected to a direct compression, without any tendency to bend, so that its brittleness, which would be detrimental under conditions of compound stress, was not here objectionable. Steel from many different manufacturers was tried, and the best grades of steel for this purpose were found to be steels which contained some chromium as well as high carbon. The compression that a piece of glass-hard steel will support when it is held rigidly so that it will not bend is surprisingly large; several grades of steel were found that would support a compression of 600,000 pounds per square inch, and one grade supported as high as 750,000 pounds per square inch. It will be noticed that these pressures are about twice as great as the highest pressures recorded in the present experiments. The problem of the strength of the piston did not, therefore, prove of difficulty.

The strength of the steel cylinders was also a factor which had to be settled by experiment, since it was found that no theory of the strength of a cylinder is of any value for very high pressures. All ordinary theories predict that no cylinder can be stressed to more than the tensile strength of the steel, no matter how thick are its walls; thus if the tensile strength of the steel is 150,000 pounds per square inch (as it is for many grades of high carbon steel), then theory predicts that it is impossible to maintain a pressure of more than 150,000 pounds per square inch in a cylinder, even with infinitely thick walls. It is, however, of no particular use to make a cylinder of more than a certain thickness, for the reason that the inside layers support most of the pressure; the outside layers of the material of a very thick cylinder do not take up the stress of the inner layers, and the cylinder flows at the inside at a certain pressure. A few rough experiments showed the actual pressure that a cylinder can support to be much in excess of that predicted by the ordinary

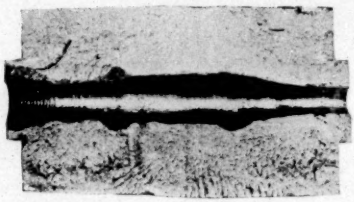
theory; this is on account of the fact that when the pressure reaches a certain value the inner layers do not break, but stretch, and thus allow the outer layers to assume some of their share of the load. It was found that the most efficient way to make a cylinder support a high pressure was first to stretch it on the inside by applying a much higher pressure than it was intended to maintain in practice, and then to machine it to its final diameter. A cylinder treated in this way is in a state of internal strain, exactly as is a gun which has hoops shrunk on it from the outside, the tension in the hoops inducing initial compression in the interior of the gun. When pressure is produced in such a gun, it removes the compression from the inner layers of the material and the tension of the outer layers is increased. But it has been shown that the tension in the inner layers increases more rapidly than that in the outer, and it can be seen, therefore, that, in time, the increasing tension in the inner layers neutralizes the compression which existed there initially and eventually equals the increasing tension of the outer layers, with the result that finally the stress throughout the mass of the cylinder is one of uniform tension. In an ideal condition all parts of the cylinder would be ready to break at the same time, and then the maximum possible strength would result; in any actual case it is, of course, impossible to reach this ideal, but, with the cylinders subjected to a preliminary stretching, it can be approached much more nearly than even in a built-up gun. There are other considerations, which need not be gone into here, which come into force when the cylinder becomes very thick. In actual practice, as already stated, very little is gained in making the cylinder of more than a certain thickness.

The best steel to use for the cylinder is found to be a steel which will stretch considerably before breaking, but which has, at the same time, a high tensile strength. The glass-hard steel used for the piston would not serve at all for this purpose, as a cylinder made of such material would inevitably crack at the inner layers, instead of stretching, and so would not allow the outer layers to assume their share of the load. The steels found most suitable are those tough steels that have been put upon the market to meet the demands of the manufacturers of automobiles. One steel made by Krupp was found very good, but best of all was a steel made in this country by the electric fur-

nace method; this steel is a chrome vanadium steel, and has, when hardened in oil, a tensile strength that may reach as high as 300,000 pounds per square inch. The highest pressure that I have ever found it possible to reach in a cylinder has been 40,000 atmospheres, or twice the highest pressures at which I have made accurate measurements.

In the preliminary work on steel cylinders many cylinders were broken. This gave opportunity for interesting observations on the manner of rupture at high pressures, and two facts not to be expected according to ordinary theories were noted. The first was the enormous amount of stretch that the steel at the inner layer of a cylinder will support without rupture; this is well shown in Figs. 1, 2, and 3. In the first figure the cylinder

FIG. 1.



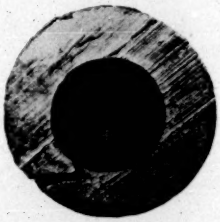
One of the halves of a cylinder of tool steel split by the application of internal pressure. The inner hole has stretched from ½ inch to 1¼ inches. The maximum pressure withstood by this cylinder was 30,000 atmospheres.

was originally one-half inch in diameter, but it stretched to one-and one-fifth inches before breaking. This same specimen of steel, if tested for tensile strength in the ordinary way, would have broken when the strain had become about 30 per cent., whereas here the strain was about 140 per cent. before the rupture took place. The second observation was that in all the cylinders tested the break started at the outside, where the stress and the strain are both least; this was observed in all the steels used. There is reason to believe, however, that very brittle substances like glass would break at the inside, as predicted by the ordinary theory. The fact seems to be that if the substance is brittle it will break at the inside first, but that if it is at all plastic it will break at the outside first, the crack travelling into the inside.

In addition to the data obtained regarding the manner in

which materials break at high pressures, many other peculiar facts were noted during these preliminary tests. Perhaps the most interesting of these is the increase in rigidity experienced in substances ordinarily soft and pliable. A striking example

FIG. 2.



Cross section of a cylinder of Bessemer steel ruptured by the application of internal pressure. This cylinder was originally 2 inches outside and $\frac{1}{2}$ inch inside diameter. The inner hole has been stretched to $1\frac{3}{4}$ inches.

of this is afforded in the case of paraffin, which under pressures as high as 20,000 atmospheres becomes more rigid than soft steel, so that if paraffin is forced to flow by the application of a very high pressure, and a piece of soft steel is imbedded in it, the steel will flow with the paraffin and will become distorted and twisted with the latter. Soft rubber also becomes very hard

FIG. 3.

View of the outside of the cylinder shown in Fig. 2, taken before the section was made.

and brittle under high pressure; in one experiment a soft rubber washer became so brittle that it cracked like glass, and a soft steel washer in contact with the rubber was forced by the pressure in ridges into the cracks in the rubber, thus showing that the rubber had become harder than the steel.

At the beginning of the experiments it was feared that the steel of the cylinder might become porous under very high pres-

sure, causing the liquid to be forced through the solid walls. No instances were found, however, in which the liquid had been forced, by pressure, into the solid metal to any appreciable depth. Many instances have occurred in which a liquid has been blown in a solid stream through apparently solid steel, but all such cases have been traced to flaws in the steel. The only apparent exception is the impossibility of retaining mercury in a cylinder under a high pressure, as the mercury invariably finds its way through the walls and usually ruptures the cylinder. The explanation of this was found to be, however, that the mercury amalgamates with the steel under high pressure, so that this is properly a case of porosity.

Another all-important task in the preliminary experiments, in addition to that of finding what pressures the steel vessels could stand, was to devise some way of accurately measuring the pressure. It need hardly be said that none of the ordinary pressure gauges are of the slightest service at these high pressures, and some means of measuring pressures other than with an ordinary gauge had, therefore, to be devised. The very simplest method that can be conceived proved to be the best in this case. It consists in inserting a steel piston through a hole in the wall of the cylinder and measuring the force necessary to prevent it from being blown out by the pressure within. There are many mechanical difficulties in realizing such a method as this, the most obvious being to overcome leakage. To do this the piston must fit the hole tightly, but at the same time must fit so freely that there is not enough friction to destroy the accuracy of the readings obtained by its means. It was found possible, by using a small-diameter piston fitting into a comparatively long hole, to take care of both these factors. With the gauge as finally constructed, pressures up to 13,000 kilogrammes per square centimetre were measured with an accuracy of one-tenth per cent. After high pressures had been successfully measured with such a gauge, it was found possible to construct gauges of a much more convenient form for actual use, and to calibrate them against this, which became an "absolute" gauge. One gauge that I have used in most of my later work is a manganin resistance gauge, which consists of a coil of manganin wire placed in the pressure cylinder and connected through insulated leads with apparatus for measuring the resistance. The electrical re-

sistance of this coil is found to change with changes of pressure in the cylinder. In the case of manganin, the resistance increases as the pressure increases, and by comparing with the absolute gauge the increase was found to be almost exactly proportional to the increase of pressure. On account of this, manganin is a very much more convenient material to use than any pure metal, since the resistance of all pure metals decreases as the pressure increases, and the decrease is, moreover, not proportional to the increase of pressure.

After the completion of the preliminary work, in which the methods of producing and accurately measuring high pressures had been decided upon, there were opened a number of interesting fields for investigation, and the question arose as to which field to choose in order to obtain the most significant results. It was at once seen that nearly any kind of measurement would involve, as one of the data needed in discussing the bearing of the results, a knowledge of the change of volume of the substance under pressure, with the pressure, and it was decided, therefore, to obtain, first of all, measurements of such changes or compressibilities.

The first substance chosen for the measurement of compressibility was water, chiefly as it is so common a substance, and because many measurements had been made on it previously at low pressures. In this connection a method was devised by which the compressibility of water could be measured up to 12,000 kilogrammes. It will be well to mention here that water is not absolutely incompressible, as is commonly supposed, but that its volume may be very appreciably diminished by the application of sufficiently high pressures. Under 12,000 atmospheres a decrease of volume of about 20 per cent. is produced. The measurements of the compressibility of water by the new method were found to be satisfactory at comparatively low pressures, but at higher pressures there were, quite frequently, discrepancies which could not be explained by errors in the apparatus. The temperature of these measurements was that of the room, about 20° C.

Apparently the only possible explanation of the irregularities shown was that the water had been frozen by the high pressure, so that measurements of the volume at high pressures were sometimes being made on the liquid and sometimes on the solid.

This explanation, if it were the true one, indicated a very remarkable state of affairs, as the application of ordinary pressures to ice causes it to melt. One would expect to be able to melt ice by high pressure, therefore, and not to freeze water. However, the above explanation does not seem so utterly improbable as this reasoning would suggest, when there is taken into consideration some remarkable work performed by Professor Tammann at Göttingen. Professor Tammann found that when ice is subjected to pressure at temperatures lower than —22° C. it is no longer possible to cause it to melt, but that, instead, it changes in form, passing over to another kind of ice which is more dense than water, instead of less dense, as is ice at atmospheric pressure. The pressure needed to produce this second kind of ice is about 2200 kilogrammes per square centimetre. These two forms of ice are comparable to the two forms of carbon-coal and diamonds, with this difference, however: this new kind of ice changes to ordinary ice just as soon as the pressure on it is removed, in the same way that ordinary ice will change into water when a sufficient amount of heat is applied. Tammann succeeded in discovering two new kinds of ice, each denser than water.

The discoveries of Tammann materially assist in providing an explanation of the irregularities found in the compressibility measurements referred to above, since, if the ice is denser than water, it may be expected that its freezing point will be raised as the pressure is increased, according to the following reasoning: First consider ordinary ice,—that is, ice at atmospheric pressure; apply pressure to it, and its volume decreases slightly. But if the ice melts, its volume also decreases. Consequently, when pressure is applied, the ice is being helped to melt, so that ice under pressure will melt at a slightly lower temperature than does ice on which there is no pressure. In the same way, if the volume of the ice be less than the volume of the water, and pressure be applied to the water, its volume would be decreased, so that water under high pressure is frozen more easily than water at atmospheric pressure. In other words, if the ice is of less density than water, the freezing point is lowered by the application of pressure, but if the ice is of greater density than water, the freezing point is raised by pressure.

The application of this proposition to the irregularities men-

tioned above is immediate. Tammann had discovered that at high pressures there are two modifications of ice, each of which is denser than water. It would be expected that the freezing point of the modified form would be raised by the application of pressure, so that possibly the irregularities could be explained by the freezing of water to this new form of ice at 20° C. under the very high pressures reached in this work, which were about five times those reached by Tammann. But the fault in this explanation is that Tammann had predicted from measurements on this new kind of ice that no pressure, however great, could possibly raise the freezing point of water higher about —17°, and a temperature of +20° C. was here being employed. Careful investigation of the whole matter was therefore called for, and special apparatus had to be designed to attack the new problem.

To state that it is possible in the experiments to ascertain whether the water has frozen to ice or not may appear strange, when it is considered that the ice is enclosed in a cylinder and can never be seen, because as soon as the pressure is removed and the cylinder opened the ice immediately liquefies. As a matter of fact, this cannot be ascertained, except indirectly. When the water freezes to ice, there is a decrease in volume, and this is shown by a drop in pressure. Conversely, too, when ice melts to water the volume increases, which is indicated by an increase of pressure.

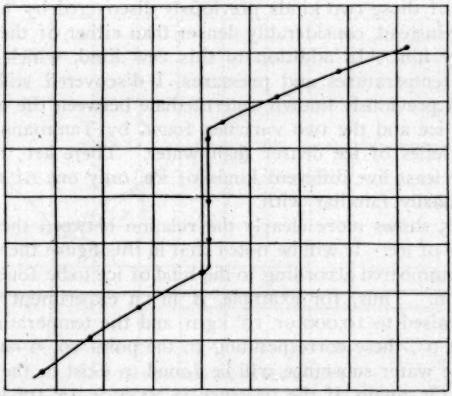
In the actual measurements the temperature of the water was kept constant. In order to increase the pressure, the piston was pushed into the cylinder, the distance being measured, and the displacement of the piston plotted against the increase of pressure produced. The pressure at first increased regularly as the displacement, but when the pressure reached a value high enough to freeze the water at the particular temperature of the experiment the volume suddenly decreased without the pressure rising at all. Then, after freezing was completed, so that there was only solid ice in the apparatus, the pressure resumed its regular rise with the displacement. This is illustrated by the curve in Fig. 4, in which the abcissæ represent pressures and the ordinates displacements.

The pressure at which the piston falls into the cylinder without producing a rise of pressure (that is, the vertical part of the

curve in Fig. 4) is the pressure at which the water freezes to ice at the particular temperature of the experiment. For every temperature, the pressure at which the water freezes is different. When the ice is denser than water, the freezing temperature increases as the pressure increases. In this way it is possible to find at what pressure water freezes for any given temperature, and so to construct so-called "melting curves."

It will be noted that the method given above, besides determining the pressure at which water freezes at a given temperature, determines another factor. The amount by which the pis-

FIG. 4.



ton is pushed in while the pressure remains constant evidently indicates the change of volume in the water while freezing, from which the difference in volume between the water and the ice can be computed. If we know the density of the water, we can calculate immediately the density of the ice. This is important data, since if both the temperature and pressure at which the ice melts are known, together with the change of volume, the amount of heat necessary to melt the ice can also be computed.

The method of experiment outlined above is not original with the writer, and has, in fact, been employed by many other previous experimenters. The only important difference is that the new packing which I devised makes it possible to obtain

a piston which has absolutely no leak, even at the highest pressures, and so renders possible accurate measurements of the change of volume. This has, I believe, not been possible before. In all previous experiments there has been some leakage around the piston, which made it impossible to obtain accurate measurements of the change of volume.

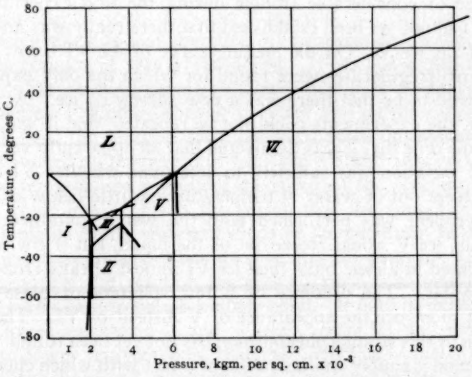
To return now to the compressibility measurements and the discrepancies found at high pressures, the application of the present method of experiment to the study of water showed that there did exist a new variety of ice at the high pressures, as had been suspected. It was found that the new variety of ice was not one of those two kinds previously discovered by Tammann, but was, instead, considerably denser than either of the varieties found by him. In addition to this new kind, which is stable at high temperatures and pressures, I discovered still another kind, not previously known, intermediate between the new high-pressure ice and the two varieties found by Tammann, making four varieties of ice denser than water. There are, therefore, in all, at least five different kinds of ice, only one of which we are ordinarily familiar with.

Fig. 5 shows more clearly the relation between these different kinds of ice. It will be noted that in this figure there are five regions, numbered according to the kind of ice to be found within the region. Thus, for example, if in an experiment the pressure be raised to 10,000 or 10^4 kgm. and the temperature maintained at 0°, these corresponding to the point 10, 0 on the diagram, the water substance will be found to exist in the form of ice VI. Or, again, if the pressure is 2000 or 2×10^3 kgm. and the temperature +20° (point on the diagram 2, 20), then the water substance is in the form of ordinary liquid water; or, thirdly, if the pressure is 1000 or 10^3 kgm., and the temperature —20° (point on the diagram 1, —20), then the water substance is in the form of ice I, the form we are ordinarily familiar with.

On any of the boundary lines of the regions in Fig. 5 the two adjacent forms of water substance are in equilibrium with each other, but if the state of the mass be changed slightly so that it is represented by a point within either of the regions, the kind of ice in that region prevails and the other disappears. Thus, let us suppose that there is ordinary ice, ice I, at say —10° and atmospheric pressure, in the apparatus at the beginning of

an experiment, then if the pressure be increased (keeping the temperature constant at —10°) at about 1000 or 10^3 kgm. (point 1, —10), the ice melts to water. But if now we continue to increase the pressure, at about 4400 or 4.4×10^3 kgm. (point 4.4, —10), the liquid water freezes again to a new kind of ice, ice V, which is denser than water. If we still further increase the pressure, at about 6300 or 6.3×10^3 kgm. (point 6.3, —10), the ice V suddenly changes to ice VI, the volume again decreasing during the change. Or, if we commence at atmospheric pressure and —30° (point 0, —30), and increase the pres-

FIG. 5.



The equilibrium diagram between the liquid and the five solid modifications of water.

sure, we first change ice I (ordinary ice) into ice III, then, on still further increasing the pressure, ice III changes to ice II; on further increase, II changes to V, and finally V changes to VI. The high temperature to which the curve between ice VI and the liquid runs is of interest; by the application of 20,000 or 20×10^3 kgm. we may freeze water, although it is nearly boiling hot.

The four varieties of ice denser than water have several interesting properties. Thus it will be noticed in Fig. 5 that the curve separating region VI from the region of the liquid, L, is prolonged into the region where V is stable. The interpretation of this is that it does not always hold that when one

of the modifications is carried into a region, in which another variety exists as the stable form, the unstable form will immediately disappear; thus it is possible to carry either liquid water or ice VI into the region in which V is the stable form, and to maintain it there for a considerable time without the change to V taking place. We are all familiar with a similar property shown by liquid water at atmospheric pressure; it is possible to cool liquid water considerably below 0° without the water freezing, particularly if care is taken not to subject the water to any mechanical disturbance. The fact that liquid water and ice VI may both exist in the region in which V is the stable form was the cause of considerable trouble during the first experiments, when it had not yet been established that there really was another form of ice, ice V. On the melting curve of ice VI below 0° a number of irregularities were found for which the only explanation seemed to be that there was a new variety of ice. At first, however, the experiments could not be repeated, and it was only after some time that it was discovered that an apparently very unessential variation was sufficient to determine whether VI or V would freeze out of water at temperatures a little below 0°. If the experiment was performed with the water contained in a glass bulb, ice V would freeze out of the liquid, but if the water was enclosed in a steel bulb, then ice VI almost always froze out of the water. The presence of a few splinters of glass was sufficient to ensure the appearance of V instead of VI. The explanation of this strange phenomenon has not yet been found. The phenomenon is simply an illustration of a fact with which chemists have been familiar for a long time; namely, that if a substance is capable of existence in two or more forms, it usually holds that the more unstable form appears instead of the stable form.

There is one exception to the statement that it is possible to carry one modification into the region of another and maintain it stable. None of the varieties of ice can be carried into the region in which liquid water is the stable form without the solid melting. It seems to be impossible to superheat a solid with respect to a liquid, although it is almost always possible to subcool a liquid with respect to a solid. This rule has been hitherto found to be of practically universal application at atmospheric pressure, and it is here seen to apply at high pressures also. Ice II behaves in a similar way with respect to ice III. Ice II may

not be superheated appreciably with respect to ice III, but III may be very considerable subcooled with respect to II. That is, III behaves with respect to II as if it were a liquid, although we know, by direct proof, that III is really a solid.

The manner in which one ice changes into another is truly remarkable. We know that water freezes slowly or that ice melts slowly, but some of these kinds of ice will change into another kind so rapidly that the reaction reminds one of an explosion. For instance, if ice I is changed to ice III at —25°, the reaction takes place so suddenly that it is impossible to follow the change of pressure which takes place after the reaction. On several occasions I have heard of a click in the apparatus when the transformation took place, so rapid was it. Still another remarkable thing is that the effect of temperature on the velocity of the reaction is very great indeed. If ice I is cooled to about —50°, the reaction occurs so slowly that it takes hours for its completion. Similar behavior is found also on the curves III–V and V–VI; the reaction from one solid form to another is very rapid indeed at temperatures near the melting temperature, but as the temperature is reduced the speed of the reaction becomes very much less. This is the reason that the curves separating the domains of the different kinds of ice could not be followed to lower temperatures than are shown in the diagram. At lower temperatures the reaction becomes so very slow that it would have taken days to obtain a single point. It is to be expected that the curves separating II and V and V from VI will continue to run to lower temperatures, that they will finally meet, and that from the point of intersection a new equilibrium curve, the curve between II and VI, will start. The point at which any three curves meet in the diagram is called a triple point. It will be noticed from the figure that two curves never meet without a third curve starting from the point of intersection of the other two. This is always true, provided that on two of the curves there is a phase in common; it may be proved mathematically that such is the case, but to prove this here would take us too far afield.

The fact that ice I gives place to ice II at a certain pressure has one practical application. We have often heard of the immense pressures developed when water is allowed to freeze in a closed vessel. Burst water pipes are a familiar example of

this, and there are also well-known experiments in which cannon balls have been split open by freezing water. It is of interest to inquire how much pressure might be reached in this way. The diagram furnishes an answer to the question, as it shows that if the pressure on the ice during freezing should rise to much over 2000 or 2×10^3 kgm., corresponding to 30,000 pounds per square inch, the ordinary ice would change to ice III, which has a much less volume, so that the ice would tend to shrink and the rise of pressure would be arrested. Thirty thousand pounds per square inch is, therefore, the highest pressure that can be obtained by freezing water in a closed space.

It may be of interest to give a rough idea of the difference of volume between the different forms of ice. To indicate the change of volume accurately, it is necessary to specify the pressure and the temperature at which the change from one variety to the other takes place, because the change of volume depends somewhat on both these factors. Roughly, ordinary ice,—ice I,—is from 10 to 13.5 per cent. less dense than water. Ice III is on the average 3 per cent. denser than water and 20 per cent. denser than ice I. Ice II is about 22 per cent. higher in density than ice I. Ice V is about 5.5 per cent. denser than ice III and perhaps 6 per cent. denser than water. Ice VI is 4 per cent. denser than ice V and from 9 to 5 per cent. denser than water.

The latent heat,—that is, the amount of the heat absorbed when ice melts to water,—is about the same for all the varieties denser than water that it is for the ordinary kind. The various modifications of the solid have, however, this remarkable relation to each other; namely, that the one may change to another in a large number of cases without any appreciable transfer of heat. Wherever, in the diagram, there is a transformation curve running vertically, then on that line the one solid form passes to the other without appreciable heat transfer. This fact allows the very sudden change from one solid form to another that has been commented on, because if there were any heat of transformation it would be set free during the reaction, and would have to be conducted away, which would take time. Therefore the reaction could not run faster than the heat could be conducted away. In those cases in which there is no heat to be conducted away the reaction might be very fast indeed. But the fact that there is no heat of transformation does not explain why the

reaction is very rapid; it simply makes a rapid reaction possible, provided that the other factors are favorable. This is shown by the fact that at the lower temperatures on the transformation curves there is still no heat of reaction, but the reaction, nevertheless, runs slowly.

A word as to the possibility of proving that the various new forms of ice that have been described are really solids. All that has been shown in the experiments is that at certain pressures and temperatures there is a sudden change of volume. This must mean a change of some kind in the molecular structure of the substance, but on what grounds can it be said that the change is a change to a solid form? May not there conceivably be two modifications of the liquid? The answer is, firstly, that no substance is known which has two modifications of the liquid, but that many are known which have two solid forms. None of our ideas of the molecular structure of solids or of liquids would lead us to think that two liquid forms of a substance are possible. Secondly, Tammann has given direct experimental proof that the two forms of ice, II and III, are really solid. He did this by cooling the cylinder containing the ice to the temperature of liquid air, and then opening the cylinder after pressure had been relieved, still keeping the temperature at that of liquid air. Of course, as soon as pressure was relieved, the ice II or III, whichever it happened to be, became unstable, but at this low temperature the reaction from the unstable to the stable, or ordinary ice, runs very slowly indeed, so that there was time enough to examine the contents of the cylinder, after opening it, before all the unstable variety had disappeared. It was found that the new substance was indeed a solid, and that as it changed into ordinary ice it increased greatly in volume. Tammann performed this experiment for both the varieties II and III. It might perhaps be possible to repeat the experiment for the other two varieties, V and VI, but the chances of success are very much less, because atmospheric pressure is so much further removed from the equilibrium pressure for these two varieties that the reaction would be expected to run very much more rapidly. What is more, the behavior of these new varieties is in all respects like that of the two varieties which we know to be solid; that is, under some conditions the reaction velocity is much greater than it ever is when a liquid passes to a solid. Also, in some cases

when one variety changes to another, enough pressure is exerted on the thin steel vessel containing the ice to rupture it. It is difficult to conceive how a liquid would develop enough pressure to rupture a steel vessel; one would expect instead that it would flow away, relieving the pressure as fast as it was formed. The overwhelming probability from all the evidence is, therefore, that the other two varieties, V and VI, are solid also.

Experiments which I have performed since these experiments on ice show that the ability to exist in more than one solid form is not confined, by any means, to water substance, but is in all probability a quite common property of matter at high pressures. I have found other modifications of six additional substances, several of them having more than two forms. One, ammonium nitrate, has five forms, the same in number as water. I am not aware that any substance has as yet been found with more than five solid forms. The equilibrium diagrams for these different substances do not bear any obvious relation to each other or to water; the diagram would seem to depend to very great degree on the individual properties of each substance.

Finally, as to a possible explanation of why a solid may have more than one form, there are two conceivable hypotheses: One is that the molecules are arranged differently in the different forms,—that is, in different space frameworks with different kinds of symmetry, so that the different solids belong to different crystalline systems. The other is that the molecules themselves are different in the different forms. For instance, it may be that when pressure and temperature have passed certain limits two or more molecules coalesce or associate and henceforth behave as one. Doubtless there will be found instances of both kinds of behavior; one might expect, however, that in the majority of cases the change in form is due to a rearrangement of the molecules, each molecule preserving its individuality. One reason for thinking that this will prove to be the case is that it is difficult to imagine how such exceedingly rapid change from one solid to another is possible if the molecules have to form new bonds with other molecules. The rapidity of reaction suggests rather that the molecules simply snap round on axes from one position of equilibrium to another. There is no way of being certain, however, what is the correct explanation in any special case, but this is a fertile subject for future investigation.

NOTES FROM THE U. S. BUREAU OF STANDARDS.

REPORT OF THE DIRECTOR OF THE BUREAU.

THE annual report of the Director of the Bureau of Standards has recently appeared. An interesting development of the work of the Bureau is the growing demand for coöperation in connection with public-service commissions, and of the technical problems connected with the regulation of public utilities. The report says:

"The report of the activities of the Bureau during the year necessarily gives but the briefest summary of its work. In no year of its history has there been as full coöperation of all divisions of the Bureau in testing and research. This coöperation has minimized the somewhat narrowing effects of a rigid division system. Each problem when studied in a broad scientific spirit leads into every specialty, so that the fullest coöperation of the entire Bureau is essential to its success. The gratifying results of such coöperation are particularly notable in the development of standards for gas, in the researches upon metals, and the methods of testing the properties of materials, in the study of electrolysis experimentally and in the field, in the structural materials investigation, and in many other cases where success depends upon many specialties.

"In no case is such coöperation more striking than in the gradual development of the public-service commission work of the Bureau. This is an outgrowth of the weights and measures activity of the Bureau, of the coöperation with the Interstate Commerce Commission, and with other regulative and inspection services, notably the wireless service, the regulation of navigation, municipal gas regulation, standardization of specifications for materials, and central-station power service. The regulation of public utilities is distinctly a measured regulation of their technical details and is efficient only as it is based upon measures and standards. Public-utility regulation simply applies measurements and standards to new fields. Such regulation is effected by the specification of measurable standards for each element so

selected as to assure efficient service; these factors may be, for example, the measure of value, quality, size, composition, quality, speed, and the like. Safety even involves measures where, for example, safety depends upon the strength of the properties of materials or upon safe speed limits.

"Such work is an extension of the general purpose of the Bureau as a whole, coöperation in all movements which have for their object increase in efficiency in all fields through measurements and standards. The three hundred or more publications of the Bureau will give a fuller account of the researches and methods by which its work is accomplished."

An interesting summary of the work of the Bureau in connection with the testing of cement is given in the report.

CEMENTS.

A total of 15,810 samples of cement were tested during the past fiscal year at the Washington, Pittsburgh, and Northampton laboratories, representing in Government purchases about 1,600,000 barrels. The work showed an increase of 15 per cent. at Washington, 40 per cent. at Pittsburgh and a decrease of 25 per cent. at Northampton due to a decrease in shipments to the Canal Zone.

Samples of cement to be used in construction of Federal buildings throughout the country and miscellaneous samples received from Government departments and the public were tested at the Washington laboratory; also cements to be used in the construction of docks and inland river improvements.

There were purchased on Government contracts 226,725 barrels of cement at 14 different mills located in Virginia, West Virginia, Maryland, Pennsylvania, New Jersey, New York, and Indiana, which were inspected at the place of manufacture. The inspection included the taking of samples, testing, and subsequent inspection of packing and shipping. This method of inspection is convenient to the purchasing office in that only standard cement is received, and it may be used immediately upon delivery; it is also economical, since fewer samples can be taken, fewer tests made, and shipments can be made immediately on any Government contract from tested stock.

At the Pittsburgh laboratory most of the routine testing was done for the War Department, complete inspection being made at

the place of manufacture. The cement for the Isthmian Canal was tested at Northampton. The decrease in shipments to the Canal Zone was caused by the completion of certain phases of the work.

Cement Specification.—In an endeavor to obtain a United States standard specification for Portland cement the Government conference of engineers from the various departments, which was successful in formulating a Government standard specification during the preceding year, was reconvened and a joint conference organized composed of representatives from the Government conference, the American Society of Civil Engineers, and the American Society for Testing Materials. While no final agreement has been reached by the joint conference, it is anticipated that a uniform specification may be agreed to during the ensuing year.

Investigations upon Cement and Concrete.—The experimental cement plant of the Bureau has been particularly active during the past year. In all 20 burns were made in the rotary kiln, part of these being of particular interest as bearing upon the effect of magnesia in Portland cement, which has been a much disputed question. The effect of difference of temperature of burns on the same raw material was also studied in the small "stack kiln," and very interesting results obtained. Before they can be considered conclusive they must be duplicated on a larger scale.

There has been conducted in the chemical and microscopical laboratory a great deal of work on the process of hydration of cements, particularly with the use of pure materials. A report of this work is now being prepared. The experimental cement plant has also devoted several weeks to work on clay, marl, and magnesite submitted by commercial interests.

Other investigations were continued or inaugurated during the year, such as a study of sand or silica cements, which is of considerable value to the Reclamation Service, which is now using this instead of Portland cement on some projects. The value of the soundness test and a proposed high-pressure steam test for determining the quality of the cement were investigated. Tests were also continued to determine the effects of heat, moisture, and pressure, separately and combined.

A granulometric analyzer and separator were developed in order to study the value of fine grinding of cements. An in-

vestigation was made to determine the sieving value of standard cement sieves. Work was continued on the investigation of volumetric changes which take place in concrete structures, owing to the temperature variations and chemical reaction during the hardening of the concrete; this information is necessary in order to properly place expansion and contraction joints to prevent cracking of concrete structures. This work has been done almost entirely in the field, experiments being made on roadways in Michigan, Connecticut, New Jersey, Pennsylvania, and Canada.

In order to determine the effect of alkali waters on cement as actually used in service an advisory committee was organized, composed of representatives from the Reclamation Service, the drainage division of the Department of Agriculture, the Cement Manufacturers' Association, and the Bureau. This committee held several meetings and organized a program of tests which included the making of some 8000 cement drain tile which are to be installed in eight badly alkaline districts in Colorado, Montana, Wyoming, Arizona, Washington, New Mexico, and Utah; also in Missouri and Minnesota for comparative purposes. These drainage tile are to be installed during the late summer of 1913.

An investigation was made to determine the failure of concrete in Bergen Hill Railway tunnel between Hoboken and Jersey City, N. J. This involves both laboratory and field tests which have not been completed.

Some work was done on the investigation of the permeability to water of structural materials, but it had to be temporarily discontinued.

A number of miscellaneous samples of stones, bricks, concrete, and building material were tested for various Government departments.

Steps were taken toward the organization of an advisory committee to outline a comprehensive coöperative program for a field survey and laboratory investigation of the stone resources of the United States. The committee is composed of representatives from the United States Geological Survey, the Bureau of Mines, the Office of Public Roads, and the Bureau of Standards. The work is to be done coöperatively by the various Government offices.

A publication was issued during the year (Technologic Paper No. 12) on the action of salts in alkali waters and sea water on cements.

COMPARISON OF THE SILVER AND IODINE VOLTAMETERS AND THE DETERMINATION OF THE VALUE OF THE FARADAY.*

By G. W. VINAL and S. J. BATES.

A FORM of iodine voltameter was devised by Washburn and Bates and described by them in the *J. Am. Chem. Soc.*, 34, p. 1341. This instrument was found to be of about the same order of reproducibility as the silver voltameter. Because of the reversibility of the reactions taking place at the anode and the cathode, and the character of the deposit which precluded the possibility of inclusions of foreign material, it seemed a desirable instrument to use in the determination of the faraday, especially since the values for this constant had heretofore been based on the silver measurements alone.

Accordingly arrangements were made for a comparison of the silver and iodine voltameters at the Bureau of Standards during the summer of 1913. The operation of the iodine voltameters was in general the same as previously described by Washburn and Bates. The silver voltameters were of the porous cup and Smith form following the usual procedure of the Bureau of Standards. Since the same current passed through the silver and iodine voltameters, the ratio of silver to iodine may be immediately calculated. As a result of ten experiments, in each of which several voltameters of both types were employed, we find the ratio

$$\frac{\text{Silver}}{\text{Iodine}} = 0.85017,$$

which is slightly higher than the ratio (0.84998) of the present atomic weights. All sources of error have been carefully examined and are critically discussed in the full paper. None, however, are believed to be sufficient to account for the difference between this value and the ratio of the present international atomic weights.

Using the results of the silver voltameter to measure the coulombs passing through the circuit according to the decision of the London Electrical Conference (1.11800 mg. of silver = 1 coulomb), the electrochemical equivalent of iodine is:

1.31502 mg. per coulomb.

* To appear in full in the *Bulletin of the Bureau of Standards* and *Journal of American Chemical Society*. Communicated by E. B. Rosa.

The value of the faraday on the basis of the present international atomic weight of iodine (126.92) and the foregoing value of the electrochemical equivalent of iodine is:

$$\frac{126.92}{.00131502} = 96{,}515 \text{ colombs.}$$

The value of the faraday derived from the atomic weight of silver and the defined electrochemical equivalent of silver is:

$$\frac{107.88}{.00111800} = 96{,}494.$$

The mean value of the two is 96,504, but we recommend for general use the round number 96,500.

THE SILVER VOLTAMETER.

PART IV.

FOLLOWING the work of the International Technical Committee at Washington in 1910, the Bureau of Standards has carried out an extended comparison of the porous cup and Smith forms of voltameter for the purpose of affording the added data necessary for the adoption of specifications for the voltameter. This work, which is about to be published by Messrs. Rosa, Vinal, and McDaniel, gives as the value for the Weston Normal Cell at 20° C. 1.01827 volts. This value justifies that adopted by the International Technical Committee (1.0183 volts). The two different forms of voltameters were found to be in good agreement, giving 1.01826_7 volts (porous cup form) and 1.01827_4 volts (Smith form).

The question of the effect of acid in the electrolyte was carefully examined. With pure electrolyte the acid causes a decrease in deposit for which a quantitative relation has been found. With impure electrolyte the results are very uncertain. Tests showed that the action of acid could not be attributed to a deposition of hydrogen ions at the beginning of the deposit, as had been suggested.

A study of the effect of septa other than filter-paper showed conclusively the danger of using silk to wrap the anode, as has sometimes been done. The porous pot, when properly prepared, is without action on $AgNO_3$.

The question of the purity of the deposit was studied, but the great experimental difficulties prevented an altogether satisfactory conclusion being reached. However, it is believed that in deposits made from very pure silver nitrate and presenting a perfect crystalline appearance the inclusions are very small.

The conditions under which the loss of weight at the anode is equal to the gain at the cathode were determined. Under favorable conditions the deposit of silver on the cathode and the loss of silver at the anode balanced to a high degree of accuracy. This would seem to disprove the existence of the secondary reactions believed by some previous observers to take place at the anode.

ELECTROLYSIS FROM ELECTRIC RAILWAY CURRENTS AND ITS PREVENTION.*

AN EXPERIMENTAL TEST ON A SYSTEM OF INSULATED RETURN FEEDERS IN ST. LOUIS.

THE paper describes a comparative test on electrolysis conditions, first under a system of uninsulated return feeders, and then under an insulated feeder system, installed at the Ann Avenue substation of the United Railways Company of St. Louis, Mo. The rated capacity of the Ann Avenue substation is 4000 kilowatts, and at the time of the test the average current during the hour of maximum load was about 7500 ampères. Only one single track passed immediately in front of the station, and one other single track passed along a street a block distant. The location was thus unfavorable to the return of current to the station, and a relatively large amount of negative copper would be required under any system.

The negative feeders were so installed that they could be operated either as insulated or uninsulated feeders, and tests were made to show the relative effectiveness and cost of the two systems.

The total weight of copper originally installed by the United Railways Company as uninsulated negative feeders was 65,630 pounds. When the system was converted to an insulated negative feeder system the weight of copper was increased to 80,720

* Abstract of Technologic Paper No. 32.

pounds to reduce the potential gradient in the rails return at all points of the system to a satisfactory value.

The bonding of the track was carefully examined and bad bonds were replaced. Tests were then made with the feeders insulated and uninsulated, the same amount of copper being used in each test.

Rail gradients were taken on a measured length of four feet of rail on all rails on both sides of each feeder tap.

The average rail gradient with uninsulated feeders was 0.91 volt for the 24-hour period, while the corresponding value for the insulated feeders was 0.47 volt.

With the assistance of the city water department and the gas company, potential wires were placed four feet apart on 14 water and 7 gas pipes at points where the current on the pipes would probably be the largest.

Readings of the millivolt drop on the pipes, and data on the size and kind of pipe, permitted the computation of the currents carried on these pipes. These measurements showed that the average current flow on the pipes when the uninsulated feeder system was in operation was 5.7 times greater than under the insulated feeder system, there being no metallic connection between pipes and rails in either case.

Potential differences between water pipes and rails were observed at a large number of points and show a marked improvement under the insulated system. The results are given under three groups. All of the points at which the pipe were more than 1 volt positive to rails under the uninsulated system average 2.35 volts under that system, and 0.22 volt with uninsulated feeders, showing a reduction in the ratio of over 10 to 1. On the other hand, eight points which averaged 0.39 volt negative to rails with uninsulated feeders showed an average value of 0.35 volt positive to rails with insulated feeders. The positive area with insulated feeders is shown to be increased, but the potential differences are nowhere high enough to be dangerous.

Twenty-two over-all potentials were measured between the tracks at the substation and the most distant feeding points of the substation. The average of those values was 10.4 volts with uninsulated and 2.6 volts with insulated feeders. The corresponding gradients in volts per thousand feet were 2.6 volts and 0.35 volt respectively.

Data are also given on the cost of the two systems, and show comparatively little difference in net cost, while a summary of the test data shows that electrolysis conditions are very much better under the insulated return feeder system than under the uninsulated system.

THE PRODUCTION OF TEMPERATURE UNIFORMITY IN AN ELECTRIC FURNACE.*

By ARTHUR W. GRAY.

AFTER discussing some fundamental principles underlying temperature control, and reviewing previous attempts to secure temperature uniformity in electric furnaces, the author shows how heat losses from the ends of a long air column may be materially lessened by means of a plug formed of two thick blocks of a good heat conductor. He then describes the development of an electric furnace in which the longitudinal temperature gradient was controlled by the use of such plugs combined with end-heating coils. Numerous illustrations make clear the construction of the furnace and accessories, and contrast the temperature distributions obtained with those obtained by other experimenters in this field.

The method has made it possible to heat a region of considerable length to any desired temperature up to 700° C. so uniformly that irregularities in the temperature distribution will be less than the effect of heterogeneity in thermo-elements of the best quality, and probably less than the uncertainties at present existing in our knowledge of the temperature scale itself.

INDUSTRIAL GAS CALORIMETRY.†

By C. W. WAIDNER and E. F. MUELLER.

AFTER an outline of the object of the investigation, precise definitions of the heat units and of the several heats of combustion are considered. After reference to the more important types of calorimeters that have been applied to the measurement

* Abstract of a paper soon to appear in the *Bulletin of the Bureau of Standards.*

† Technologic Paper of the Bureau of Standards.

of the heating values of gases, the principle of the flow calorimeter is set forth, and an example is given showing the reductions of and corrections to the observed data that are required in order to find the total and net heating values.

The results of an experimental investigation of laboratory gas meters, showing the errors to which such meters are liable, the precautions to be observed, and the accuracy attainable in their use, are given at length. It is shown that an accuracy of about 0.2 per cent. may be attained if the meter is calibrated *in situ* at the time of use, and that the calibration may be reproduced from time to time, by making suitable adjustments, to an accuracy of about 0.5 per cent.

The results are given of an extended series of investigations of the various factors that may affect the accuracy of heating value determinations with flow calorimeters, such as: completeness of combustion; accuracy of the temperature measurements; the magnitudes of the various heat losses from the calorimeter, particularly as affected by the volume of the entering air and of the products of combustion and by the atmospheric humidity; and the accuracy of measurements of the quantities of water and of gas. The effects of certain other factors, which depend on the nature of the gas tested and are particularly noticeable in the testing of illuminating gas, are briefly considered.

The results are given of an extended series of experiments with natural gas and with nearly pure hydrogen which show that, when the necessary corrections for losses of heat from the surface, for the effect of atmospheric humidity, etc., were applied to the observed heating values obtained with flow calorimeters of suitable design and construction, the total heating values thus found were in agreement to about 0.3 per cent. with the total heating value obtained with calorimeters of the Berthelot bomb type, provided due allowance were made for the difference between the heat of combustion at constant pressure and the heat of combustion at constant volume. The results obtained with illuminating gas indicated that the heating values obtained with the Berthelot bomb type of calorimeter were probably in error, being too low (about 1 per cent.), but further investigation will be required to determine the cause of the discrepancy found.

The summarized results are given of a critical investigation of eight flow calorimeters, representing types widely used in

this country or abroad, and of one calorimeter of the comparison type.

The investigation has shown that several of the calorimeters that were investigated could be used, when proper precautions were observed and suitable corrections were applied to the observed heating values obtained with them, to determine the total heating values of most kinds of gases to an accuracy of about 0.3 per cent. Some of the calorimeters are, however, subject to constant errors that cannot be eliminated or be readily determined except by comparison with a standard instrument, such errors for one calorimeter amounting to nearly 2 per cent.

Examination of a very large amount of data obtained during the investigation indicates that with those calorimeters free from significant constant errors total heating values should be determinable, under conditions obtaining in the practical testing of gas, to an accuracy of the order of 1 per cent.

STANDARD DENSITY AND VOLUMETRIC TABLES.*

A new and somewhat enlarged edition of Circular No. 19, of the Bureau of Standards, is soon to appear. An idea of the scope of the tables included in this circular may be gained from the outline which follows:

Table 1 gives the density of water (according to P. Chappuis) at every tenth of a degree from 0° to 40° C.

Tables 2 to 8, inclusive, are standard density and specific gravity tables for ethyl alcohol. They are based on work done at this Bureau and published in Vol. 9, No. 3, of the Bulletin of the Bureau of Standards (Reprint No. 197).

Tables 9 to 11 are similar tables for methyl alcohol. They are based on the work of Doroshevskii and Rozhdestvenskii.

Tables 12 and 13 are density tables for sugar solutions.

Tables 14 and 15 are density tables for sulphuric acid solutions.

Tables 16 to 19 give the relation between specific gravity and degrees Baumé in use in the United States.

Table 20 is for changing the density basis of hydrometers and picnometers.

* Circular No. 19, 4th edition.

Table 21 gives the weight of a litre of air at various pressures and temperatures.

Table 22 gives the difference between the weight of 1 c.c. of water *in vacuo* and in air at various pressures and temperatures.

Table 23 gives the apparent weight of various volumes of water at various temperatures when weighed against brass weights in air.

Table 24 gives the temperature correction for glass volumetric apparatus.

Tables 25 to 37 give the corrections to be applied to the weight of water, in air, to give the capacity of glass volumetric apparatus.

Table 38 gives the density of water (according to Thiesen) at temperatures from 0° to 102° C.

Tables 39 and 40 are master scales for the graduation of hydrometers to indicate percentages of ethyl alcohol by weight and by volume and percentages of "proof spirit."

König's New Process for the Manufacture of Cellulose. A. Frohberg. (*Wochenbl. Papierfab.*, xliv, 4432.)—In König's process, owing to the action of the sulphuric acid, the production of sugar would amount to 10 to 17 per cent. of the wood, or even more, whereas in the sulphite process it is never more than 7 per cent. Consequently the yield of cellulose by the new process would be lower and in quality it would be of the nature of a hydrocellulose. The consumption of steam in the digestion would be four times as great as in the digestion by the sulphite process. The total time occupied in the digestion and the cycle of attendant operations would be 27 hours, as against 14 to 20 hours by the sulphite process. Taking the cost of materials and steam per ton of unbleached cellulose, König's process would require an expenditure of about $60, including costs of evaporation and recovery, from which must be deducted $18.50 for the value of useful by-products (resin, tannin, and fodder-material) recovered, while the similar costs of the sulphite process, without recovery, would amount to about $27.50 per ton.

Fertilizers Containing Acid Phosphate and Calcium Cyanamide. R. N. Brackett. (*J. Ind. Eng. Chem.*, v, 933.)—Laboratory experiments and experience on a factory scale both show that in mixed fertilizers containing one part of calcium cyanamide to 6.25 or 8.33 parts of acid phosphate (super-phosphate), with or without "ammoniates" and potash salts, there is a gradual increase of the insoluble and decrease of the available phosphoric acid on standing.

THE FRANKLIN INSTITUTE

(Proceedings of the Stated Meeting held Wednesday, February 18, 1914.)

HALL OF THE FRANKLIN INSTITUTE,
PHILADELPHIA, February 18, 1914.

PRESIDENT WALTON CLARK *in the Chair.*

Additions to membership since last report, 10.

The standing committees of the year 1914–15 were announced.

Following the meeting of the Institute for the transaction of this business, a joint meeting was held with the Illuminating Engineering Society.

Dr. George A. Hoadley, chairman of the Philadelphia Section of the Society, introduced Dr. Herbert E. Ives, of Philadelphia, who presented an interesting communication on "Artificial Daylight."

The speaker discussed the problem of producing artificial light of daylight color and quality.

Various systems of color measurement were described as applied to daylight and artificial light.

Artificial daylight was produced by several methods, and its use in the industries considered at length.

An artificial daylight producer was exhibited which can be used with the Welsbach light, or, with a slight modification, with the tungsten electric lamp. A new glass was also shown for the first time, which makes possible the converting of the light of the gas mantle into true daylight.

Lantern slides were used to further illustrate the subject.

In the discussion which followed the presentation of the paper, Messrs. Bond, Henderson, Calvert, Hornor, and others participated.

After a vote of thanks to the speakers, the meeting adjourned.

R. B. OWENS,
Secretary.

STANDING COMMITTEES, 1914.

Of the Board of Managers.

INSTRUCTION.

Lawrence T. Paul, *Chairman,*
Edw. V. McCaffrey,
George A. Hoadley,
James S. Rogers,
Harry F. Keller.

ELECTIONS AND RESIGNATIONS.

W. C. L. Eglin, *Chairman,*
J. J. Gibson,
Robert Perry,
Alex. P. Robinson,
George D. Rosengarten.

STOCKS AND FINANCE.

Walton Forstall, *Chairman,*
Cyrus Borgner,
Alfred C. Harrison,
Richard Waln Meirs,
E. H. Sanborn.

PUBLICATIONS.

Louis E. Levy, *Chairman,*
John Birkinbine,
W. C. L. Eglin,
George A. Hoadley,
E. H. Sanborn.

EXHIBITIONS.

John Birkinbine, *Chairman,*
Francis T. Chambers,
E. Goldsmith,
C. A. Hexamer,
Marshall S. Morgan.

SECTIONAL ARRANGEMENTS.

Charles Day, *Chairman,*
Harry F. Keller,
Robert W. Lesley,
Louis Levy,
Lawrence T. Paul.

ENDOWMENT.

Henry Howson, *Chairman,*
James M. Dodge,
Alfred C. Harrison,
Richard Waln Meirs,
Coleman Sellers, Jr.

EXECUTIVE.

E. H. Sanborn, *Chairman,*
James M. Dodge,
Walton Forstall,
Alfred C. Harrison,
Richard Waln Meirs.

Of the Institute.

COMMITTEE ON LIBRARY.

Robert H. Bradbury,
E. V. d'Invilliers,
Richard Gilpin,
Clarence A. Hall,
Harry F. Keller,
Gaetano Lanza,
Henry Leffmann,
Louis E. Levy,
Marshall S. Morgan,
George F. Stradling.

COMMITTEE ON MEETINGS.

G. S. Barrows,
G. H. Clamer,
Geo. R. Henderson,
H. A. Hornor,
Herbert E. Ives,
M. M. Price,
James S. Rogers,
Geo. D. Rosengarten,
Coleman Sellers, Jr.

COMMITTEE ON MUSEUMS.

Henry F. Colvin,
Charles Day,
James M. Dodge,
Richard Gilpin,
George A. Hoadley,
Harry F. Keller,
Wilfred Lewis,
A. E. Outerbridge, Jr.,
Wm. H. Thorne,
Wm. J. Williams.

COMMITTEE ON SCIENCE AND THE ARTS.

(Abstract of Proceedings of the Stated Meeting held Wednesday, February 4, 1914.)

HALL OF THE FRANKLIN INSTITUTE,
PHILADELPHIA, February 4, 1914.

DR. GEO. A. HOADLEY, *Chairman pro tem.*

Mr. George R. Henderson was unanimously elected Chairman for the year 1914.

The following reports were presented for final action:

No. 2524.—Sperry's Gyro-Compass. John Scott Legacy Medal and Premium recommendation adopted.

No. 2530.—Stumpf's Una-Flow Engine. Referred back.

No. 2534.—Reno's Escalator. John Scott Legacy Medal and Premium recommendation adopted.

No. 2542.—Batdorf's Coin Counting and Wrapping Machine. John Scott Legacy Medal and Premium recommendation adopted.

No. 2587.—Spielman's Cloth Cutting Machine. John Scott Legacy Medal and Premium recommendation adopted.

The following report was presented for first reading:

No. 2541.—Guillaume's Invar.

Adjourned.

R. B. OWENS,
Secretary.

SECTIONS.

Section of Physics and Chemistry.—A stated meeting of the section was held in the Hall of the Institute on Thursday, January 29, 1914, at 8 P.M., with Dr. George A. Hoadley in the chair. The minutes of the previous meeting were read and approved.

W. P. Mason, C.E., M.D., LL.D., Professor of Chemistry, Rensselaer Polytechnic Institute, Troy, N. Y., delivered a lecture entitled "Advantages and Disadvantages of Water Storage." It was demonstrated that still water rather than running water offers the better conditions for self-purification. Examples of lake pollution of unusual type were given, and the methods of study of the influence of possible sources of pollution on water supply were described. The removal of algæ from water by means of cupric sulphate was also discussed. The lecture was illustrated by means of lantern slides.

After an extended discussion of the various phases of water storage, contamination, and purification, the meeting adjourned.

JOSEPH S. HEPBURN,
Secretary.

MEMBERSHIP NOTES.

Elections to Membership.

(Stated Meeting, Board of Managers, February 11, 1914.)

RESIDENT.

MR. SAMUEL J. CASTNER, 1631 Walnut Street, Philadelphia.
MR. SABIN W. COLTON, JR., 328 Chestnut Street, Philadelphia.
MR. CHARLES GOBRECHT-DARRACH, 5825 Willows Avenue, Philadelphia.
MR. W. H. LLEWELLYN, 1518 Chestnut Street, Philadelphia.
MR. AUSTIN G. MAURY, Northeast corner Chestnut and Third Streets, Philadelphia.
MR. HORACE B. SMITH, 3206 Higbee Street, Wissinoming, Pa.

NON-RESIDENT.

MR. A. C. HOWARD, United Gas and Electric Engineering Corporation, 37–39 Pine Street, New York.
MR. FRANK W. SMITH, Vice-President, The United Electric Light and Power Company, 1170 Broadway, New York.

ASSOCIATE MEMBERS.

MR. PENROSE R. HOOPES, Autocar Works, Ardmore, Pa.
MR. MARSHALL MILLER, Powers, Weightman & Rosengarten, Ninth and Parrish Streets, Philadelphia.

Changes of Address.

PROF. J. D. BALTIMORE, 505 U Street, N. W., Washington, D. C.
MR. JOHN CALDER, International Motor Company, Detroit, Mich.
MR. FRED A. DELANO, 1414 Transportation Building, Chicago, Ill.
MR. L. J. R. HOLST, Hotel Hampton, 112 North Eighteenth Street, Philadelphia.
MR. A. S. KREBS, 806 Franklin Street, Wilmington, Del.
MR. PEDER LOBBEN, Skobdo, Pr. Kraakstad, Norway.
MR. JOHN W. TOWNSEND, 825 Montgomery Avenue, Bryn Mawr, Pa.
MR. J. S. WHITNEY, 33 South Sixteenth Street, Philadelphia.

NECROLOGY.

William D. Marks, consulting mechanical engineer, honorary life member of the Institute, was born in St. Louis in 1849. He was educated at Yale University, and was graduated as Bachelor of Philosophy in 1870, and Civil Engineer in the following year. Until 1876 he was engaged in practical engineering work in connection with railway and gas and iron works, when he became instructor in mechanical engineering at Lehigh Unversity. In 1876 he was appointed Whitney Professor of Dynamical Engineering at the University of Pennsylvania. He was superintendent of the 1884 International Electrical Exhibition of The Franklin Institute, to the great success of which he greatly contributed. In 1887 he was appointed engineer and president of

the Edison Electric Light Company of Philadelphia. His later years were devoted to consulting work.

Professor Marks was a member of the American Institute of Electrical Engineers and a member of the American Philosophical Society. He was the author of a number of books and papers on mechanical and engineering subjects, and a frequent contributor to the JOURNAL OF THE FRANKLIN INSTITUTE.

Mr. Elijah R. Benham, 6 Central Avenue, New London, Conn.

Mr. Otto Moessner, Twenty-first Street and Fairmount Avenue, Philadelphia, Pa.

LIBRARY NOTES.

Purchases.

American Society for Testing Materials.—Proceedings 16th Annual Meeting. 1913.

CAMPBELL, N. R.—Modern Electrical Theory. 1913.

CUSHING, H. C., and SMITH, F. W.—Electric Vehicle Handbook. No date.

DYSON, C. W.—Screw Propellers. 2 volumes. Vol. 1, Text. Vol. 2, Atlas. 1913.

FULLER, H. C.—Qualitative Analysis of Medicinal Preparations. 1912.

GILDEMEISTER, E., and HOFFMAN, F.—The Volatile Oils. 1913.

GULLIVER, G. H.—Metallic Alloys. 1913.

HYDE, F. S.—Solvents, Oils, Gums, Waxes. 1913.

LANGBEIN, G.—Complete Treatise on the Electro-Deposition of Metals. 1913.

MACINTIRE, H. J.—Mechanical Refrigeration. 1914.

MARKHAM, E. R.—Steel, its Selection, Annealing, Hardening, and Tempering. 1913.

MAUBORGNE, J. O.—Practical Uses of the Wave Meter in Wireless Telegraphy. 1913.

New Hampshire Public Service Commission.—2nd Annual Report. 1912.

PALMER, R. H.—Foundry Practice. 1912.

PARKER, P. A. M.—Control of Water. 1913.

PORRITT, B. D.—Chemistry of Rubber. 1913.

PUTNAM, X. W.—Gasoline Engine on the Farm. 1913.

RICHARDS, F.—Compressed Air Practice. 1913.

RIPPER, W.—Heat Engines (being a new edition of "Steam"). 1913.

ROBERTS, C., and SMITH, R. M.—Practical Locomotive Operating. 1913.

SCHULTZ, G. and J. P.—Farbstofftabellen. 1911–13.

TILLMANS, J.—Water Purification and Sewage Disposal. 1913.

ZEEMAN, P.—Researches in Magneto-optics. 1913.

Gifts.

American Railway Master Mechanics' Association, Proceedings, vol. 46, 1913. Chicago, 1913. (From the Association.)

American Society of Heating and Ventilating Engineers, Transactions, vol. 18, 1912. New York, 1913. (From the Society.)

Boston Transit Commission, 19th Annual Report, 1913. Boston, 1913. (From the Commission.)

Boullanger, Experiences et Observations Sur le Spath-vitreux, on Fluor Spathique. 1773. (From Dr. Henry Leffmann.)

Carnegie Institution of Washington, Year Book No. 12, 1913. Washington, D. C., 1913. (From the Institution.)

Case School of Applied Science, Catalogue 1913–1914. Cleveland, 1913. (From the School.)

Columbia University in the City of New York: Publication No. 7 of the Ernest Kempton Adams Fund for Physical Research, Neuere Probleme der Theoretischen Physik, by W. Wien. Leipzig, 1913. (From the University.)

Connecticut Bureau of Vital Statistics, 65th Registration Report. Hartford, 1913. (From the Bureau.)

Engineering Society of Shanghai, Proceedings, vol. 12. Shanghai, China, 1913. (From the Society.)

Iron and Steel Institute, Journal, vol. 88, 1913, part 2, and List of Members, 1914. London, 1913 and 1914. (From the Institute.)

Joseph Dixon Crucible Company, Graphite, 1913. Jersey City, 1913. (From the Company.)

Lake Superior Mining Institute, Proceedings, vol. 18, 1913. Ishpeming, 1913. (From the Institute.)

Leland Stanford Junior University, Annual Report of the President, 1913. Stanford University, Cal., 1913. (From the University.)

Maine State Department of Labor and Industry, 1st Biennial Report, 1911–1912. Augusta, 1913. (From the Department.)

Master Builders of the World's Greatest Structure. New York, 1913. (From Mr. Richard Gilpin.)

Master Car Builders' Association, Proceedings, vol. 47, 1913, parts 1 and 2. New York, 1913. (From the Association.)

Mellon Institute of Industrial Research, University of Pittsburgh: Smoke Investigation Bulletin No. 5, The Meteorological Aspect of the Smoke Problem, by H. H. Kimball. Pittsburgh, 1913. (From the University.)

Mount Holyoke College, Catalogue 1913–1914. South Hadley, Mass., 1914. (From the College.)

New Jersey Geological Survey, Bulletins 2–4, 6–11. Trenton, 1911–1913. (From the Survey.)

New York State Education Department, State Museum Report, 65th, 1911, vols. 1–4. Albany, 1913. (From the State Library.)

Pennsylvania Life, Fire and Marine Insurance Report, 1912. Harrisburg, 1913. (From the State Librarian.)

Pennsylvania Lines West of Pittsburgh, A History of the Flood of March, 1913. Pittsburgh, 1913. (From the Pennsylvania Railroad Company.)

Pennsylvania Topographic and Geologic Survey: Report for 1910–1912 and Report No. 6, Commission Graphite Deposits of Pennsylvania, by B. L. Miller. Harrisburg, 1912. (From Dr. E. V. d' Invilliers.)

Philadelphia Bureau of Surveys, Annual Report, 1912. Philadelphia, 1913. (From the Bureau.)

Philadelphia Steam Heating Company, Catalogue. Philadelphia, 1914. (From the Company.)

Philippine Islands Bureau of Education, 13th Annual Report of the Director. Manila, 1913. (From the Bureau.)

Princeton University, Catalogue 1913–1914. Princeton, 1913. (From the University.)

Royal Astronomical Society of Canada, The Observer's Handbook for 1914. Toronto, 1914. (From the Society.)

St. Andrew's Society of Philadelphia, Historical Catalogue, vol. 2, 1749–1913, compiled by Robert B. Beath. Philadelphia, 1913. (From the Compiler.)

St. Louis and San Francisco Railroad Company, 16th Annual Report, 1912. St. Louis, 1912. (From the Company.)

Shepard Iron Works, Catalogue of Perry & Lay Compound Engine. Buffalo, no date. (From Mr. John T. Morris.)

United States Brewers' Association, Year Book 1913. New York, 1914. (From the Association.)

United States Coast and Geodetic Survey: Special Publication No. 17, Triangulation on the Coast of Texas, from Sabine Pass to Corpus Christi Bay. Annual Report of the Superintendent, 1913. Washington, D. C., 1913. (From the Survey.)

University of Cincinnati, Annual Catalogue, 1913–1914. Cincinnati, 1914. (From the University.)

University of Illinois, Reports of the Registrar and Comptroller, June 30, 1913. Urbana, 1913. (From the University.)

University of Oklahoma, General Catalogue 1912–1913. Norman, 1913. (From the University.)

University of Virginia, Catalogue 1913–1914. Charlottesville, 1914. (From the University.)

Victoria and Albert Museum, South Kensington, Catalogue of the Mechanical Engineering Collection in the Science Division, parts 1 and 2. London, 1907 and 1908. (From Mr. Edward H. Sanborn.)

Wellesley College, Calendar 1913–1914. Wellesley, Mass., 1914. (From the College.)

BOOK NOTICES.

A TREATISE ON QUANTITATIVE INORGANIC ANALYSIS, with Special Reference to the Analysis of Clays, Silicates and Related Minerals—being Volume One of a Treatise on Ceramic Industries. By J. W. Mellor, D.Sc. 778 pages, illustrations, plates, 8vo. London, Charles Griffin & Co., Ltd.; Philadelphia, J. B. Lippincott Company, 1913.

This work is accurately described by its title. It becomes at once a standard work in this special line of ceramic chemistry, as it seems to fully cover the field. The amount of text, considerable as it is found to be, is not a measure of the vast amount of material collected, as there are footnotes on nearly every page that seem to be satisfactory in their completeness.

Pages 1 to 151 are devoted to general operations under 77 headings,

and go very fully into gravimetric and volumentic processes, volumentic analysis, colorimetry, filtration and washing, heating and drying, sampling and reagents.

The body of the book is devoted to the chemical analysis of all the constituents of clays and materials, such as enamels and glazes. Of course, this very nearly covers the field of inorganic chemistry, and special methods for the estimation of elements, such as molybdenum, tungsten, niobium, tantalum, selenium, beryllium, vanadium, and uranium are given.

The third section of the work is the appendix, which is headed by a quotation from J. C. Maxwell, "The human mind is seldom satisfied, and is certainly never exercising its highest functions when it is doing the work of a calculating machine." The author has endeavored to keep the reader from doing any detail work of this kind, by doing it all himself, as he has given a number of conversion tables for calculating weights of precipitates to substances sought. It is probable, however, that every analyst has a slightly different system, and Dr. Mellor's would not fit in all cases.

There is a carefully-selected bibliography, and good name and subject indices are supplied. Very many of these methods would apply to other lines of analytical work than those which belong to the ceramic industries.

S. S. SADTLER.

THE GYROSCOPE. By F. J. B. Cordeiro, author of "The Atmosphere," "Barometrical Heights," etc. 105 pages, illustrations, 12mo. New York, Spon & Chamberlain, 1913. Price, in cloth binding, $1.50.

Within the last two or three decades the gyroscope has found various practical applications, and this has naturally stimulated interest in the study of the perplexing freaks of this instrument. This interest is met by the monograph "Gyroscope," by F. J. B. Cordeiro.

In this treatise gyroscopic reactions are treated as essentially of the nature of centrifugal force. This is true in so far as both the gyroscopic force and centrifugal force are reactions attending a change of the direction of moving bodies.

The subject is treated both in its mathematical and practical aspects, and its applications to astronomy and meteorology, as well as to the mechanic arts, are fully discussed.

HUGO BILGRAM.

NOTIONS FONDAMENTALES DE CHIMIE ORGANIQUE, par Charles Moureu, Professeur a l'École supérieure de Pharmacie de l'Université de Paris. Gauthier-Villars, Paris. 383 pages, 23 x 14 cm. Price, 9 francs.

Something like two hundred thousand compounds of carbon are known at present, and the problem of selecting the indispensable things for the beginner, out of the vast accumulation, is one of increasing difficulty. The present book is an excellent elementary account of the subject of organic chemistry. It possesses, in a high degree, that clearness and precision of statement which is such an excellent characteristic of French scientific writing. It differs, however, from many French books, in the fact that Professor Moureu is entirely familiar with the recent developments in his subject. There is an excellent account of Fischer's work on the sugars, and his researches on the

purin nucleus and on the polypeptides are briefly but clearly sketched. Important recent work, like the synthesis of caoutchouc, Grignard's organomagnesium compounds, Harries's ozonides of the olefines, and the diazomethane derivatives, receives brief but clear and adequate treatment.

The book is beautifully printed. The reviewer notes, with especial pleasure, the use of a matte-finish paper which suppresses the reflections that commonly dazzle and annoy. This is a French custom that might, with great advantage, be imitated by publishers of other nationalities. There is a good index. An English translation of this book would fill a gap in our own literature. There is no small work on the subject which covers the ground in such a thoroughly satisfactory way.

ROBERT H. BRADBURY.

THE MECHANICAL ENGINEER'S REFERENCE BOOK. A Hand-book of Tables, Formulas, and Methods for Engineers, Students, and Draftsmen, by Henry Harrison Suplee, B.Sc., M.E. 4th edition, revised and enlarged. 964 pages, illustrations, 12mo. Philadelphia, J. B. Lippincott Company, 1913. Price, $5.

The fourth edition of this book is a beautiful specimen of the work of the typographer and bookbinder. The type, tables, and sketches are very attractive and easily read, and the thumb index for turning instantly to the various sections will commend itself to those who wish to find the general subjects without searching the index for some individual title.

While this book naturally bears many of the ear-marks of an engineer's hand-book, yet it has a distinct individuality of its own in many ways. It is rather unusual, for instance, to find in the trigonometrical tables values of the versed sine and cosine. These are very useful and save the time of making subtractions. The general trigonometrical and integral formulas are very clearly printed and in very convenient form; the same may be said of the formulas for acceleration and retarded motion, as these are so tabulated that they can be readily selected to suit the desired case. The tables are given in both the English and metric units, which is a distinct advantage, now that metric measurements are being so much used. The formulas for rotary motion and those of work in moving and revolving bodies are given with a great variety of constants so that the proper form can be selected without reductions.

We are rather surprised, however, to find the old laws of friction as exposed by Morin are still adhered to; whereas we know, and particularly from the M. C. B. brake tests, that the coefficient of friction does depend very largely upon the areas in contact. It would seem that these should have been rewritten in the light of modern experiments.

The sketches showing pipe fittings, valves, etc., are very convenient for designing pipe work. When it comes to the tables of structural sections, we are rather surprised to see the Pencoyd shapes alone illustrated and no reference made to the Carnegie sections, which are much more generally used by engineers than the Pencoyd; neither do we find any reference to the Bethlehem special beam and H sections. The spring formulas also do not show the general method of making springs, but seem to have been taken bodily from Reuleaux without being modernized to suit present practice.

The strength of gears is shown only for cast iron and steel, whereas many forms of metal are used, and it seems as if the coefficients given would be too high for good practice, such as in cranes and other important gearing. The efficiency diagram, however, is very interesting and useful.

In connection with the heat given out by iron pipes as in steam heating, there are values given for still air and moving air, but the latter must be considered as moving with a very low velocity, as the values are only about 30 per cent. greater than with still air, and it is well known that when the air is forced over the pipes by means of a fan we get values four to six times as great as with still air, and this is liable to be misunderstood from the tables given.

The tables of hyperbolic logarithms are for quite a large range and in very convenient type; but the locomotive data are limited to about a page and a half, and no formulas are given for tractive power of other than simple locomotives. It seems as if this locomotive data could have been extended and enlarged with advantage to this subject.

The record of electric motor tests will be found very interesting and useful in determining the amount of power needed for machine shops and similar propositions, and the chapter on the cost of power, giving the results of various kinds of fuel and electric drives, is particularly useful for comparison. The insertion of entropy tables in a work of this kind is rather unusual, and several pages are given to an explanation of the entropy-temperature diagram.

The book as a whole will be extremely useful to engineers, and seems to cover a very wide range of subjects, more so, perhaps, than any of the other hand-books which we have in mind at the present time.

GEORGE R. HENDERSON.

LES CLASSIQUES DE LA SCIENCE. Publiés sous la direction de MM. H. Abraham, H. Gautier, H. Le Chatelier, J. Lemoine. Paris, Librairie Armand Colin, 1913.

No. 1. L'Air, L'Acide Carbonique et L'Eau. Mémoires de Dumas, Stas, et Boussingault. Avec 4 planches hors texte.

No. 2. Mesure de la Vitesse de la Lumière, Étude Optique des Surfaces. Mémoires de Léon Foucault. Avec 3 planches hors texte.

No. 3. Eau Oxygenée et Ozone. Mémoires de Thénard, Schoenbein, De Maringnac, Soret, Troost, Hautefeuille et Chappuis.

No. 4. Molécules Atomes et Notations Chimiques. Mémoires de Gay-Lussac, Avogadro, Ampère, Dumas, Gaudin, Gerhardt. Avec 1 planche hors texte.

The idea of publishing at popular prices this new series of the classics of physics and chemistry was evidently suggested by publications in other languages, particularly the comprehensive and most successful collection which Ostwald began in 1889 under the similar title "Klassiker der Exakten Wissenschaften."

As has been frequently said, the most profitable and stimulating collateral reading for scientific students is that of the original memoirs by the great investigators and discoverers. Any teacher who has succeeded in interesting his pupils in this kind of literature could not fail to notice its effect in broad-

ening and promoting their scientific understanding. The present collection is, of course, primarily intended for the French-speaking student, and for this reason it is but natural that it consists for the most part of reprints of memoirs which were originally written in French. In this respect it differs from the Ostwald series, and it also has a more pronounced national flavor than, for example, the excellent "Alembic Club Reprints" of chemical classics. But this is hardly a defect from the foreign reader's point of view; for the collection thus affords an admirable supplement to the corresponding publications in other languages. In addition to the excellently selected memoirs, each little volume contains short biographical notices of their authors, as well as fine fac-simile reproductions of the illustrations. Considering the very moderate price at which these little books are offered, their appearance is most attractive. Type, paper, and illustrations are decidedly better than those of the similar German and English publications.

H. F. KELLER.

PUBLICATIONS RECEIVED.

Die Entdeckung des Radiums, Rede gehalten am 11 Dezember, 1911, in Stockholm, bei Empfang des Nobelpreises für Chemie von Mme. P. Curie. Autorisierte Deutsche Ausgabe mit 5 Abbildungen. 28 pages, 8vo. Leipzig, Akademische Verlagsgesellschaft m. C. H., 1912.

Letzte Gedanken von Henri Poincaré, mit einem Geleitwort von Wilhelm Ostwald. Übersetzt von Dr. Karl Lichtenecker. 261 pages, portrait, 12mo. Leipzig. Akademische Verlagsgesellschaft m. b. H., 1913.

Der Werdegang einer Wissenschaft Sieben gemeinverständliche Vorträge aus der Geschichte der Chemie von Wilhelm Ostwald. 2 vermehrte und verbesserte Auflage der "Leitlinien der Chemie." 316 pages, 12mo. Leipzig, Akademische Verlagsgesellschaft m. b. H., 1908.

Die elektrolytische Alkalichloridzerlegung mit festen Kathodenmetallen herausgegeben von Dr. Jean Billiter, Privatdozent an der Universität Wien. II Teil Beschreibung ausgeführter Anlagen usw. 182 pages, illustrations, 8vo. Halle (Saale), Wilhelm Knapp, 1913. Price, in paper, 9.60 marks.

Cours de Mécanique professé a l'École Polytechnique par Leon Lecornu, membre de l'Institut, Inspecteur Général des Mines. Tome I. 536 pages, illustrations, 8vo. Paris, Gauthier-Villars, 1914. Price, in paper, 18 francs.

Industrial Chemistry for Engineering Students, by Henry K. Benson, Ph.D., Professor of Industrial Chemistry in the University of Washington. New York, The Macmillan Company, 1913.

Das Werden der Welten von Svante Arrhenius. Aus dem Schwedischen übersetzt von L. Bamberger. 9 bis 13 Tausend mit 60 Abbildungen im Text. 231 pages, 8vo. Leipzig, Akademische Verlagsgesellschaft, 1913.

Über neuere thermodynamische Theorien (Nernstsches Wärmetheorem und Quantenhypothese), Vortrag gehalten am 16 Dezember, 1911, in der Deutschen Chemischen Gesellschaft in Berlin, von Dr. Max Planck. 34 pages, 12mo. Leipzig, Akademische Verlagsgesellschaft m. b. H., 1912.

U. S. Geological Survey: Mineral Resources of the United States, Calendar Year 1912. Part 1, Metals. 1079 pages, 8vo. Washington, Government Printing Office, 1913.

Annuaire pour l'an 1914 publié par le Bureau des Longitudes avec des notices scientifiques. 502 pages, with appendices, 16mo. Paris, Gauthier-Villars, no date. Price, in paper, 1.50 francs.

Canada Department of Mines: Magnetic Occurrences along the Central Ontario Railway, by E. Lindeman. 23 pages, plates, maps, 8vo. Austin Brook Iron-Bearing District, New Brunswick, by Einar Lindeman, M.E. 15 pages, illustrations, plates, maps, 8vo. Ottawa, Government Printing Bureau, 1913.

U. S. Weather Bureau: The Floods of 1913 in the Rivers of the Ohio and Lower Mississippi Valleys, Bulletin Z, by Alfred J. Henry, Professor of Meteorology. 117 pages, illustrations, plates, maps, quarto. Washington, Government Printing Office, 1913. Price, 40 cents.

Harrison Safety Boiler Works: Cochrane Separator Catalog No. 550, Introduction and General Description. 36 pages, illustrations, 8vo. Philadelphia, Harrison Safety Boiler Works, 1913.

A Legislative Program to Restore Business Freedom and Confidence. An address delivered before the Illinois Manufacturers' Association at the Hotel LaSalle, Chicago, January 5, 1914, by Samuel Untermyer, of New York. 40 pages, 8vo. New York, 1914.

Mauro and his Rôle in Spanish Politics: Synthetic and Documental Exposition of the Ideas and Work of the Conservative Leader by an Impartial Spectator. English edition. 36 pages, 12mo. Madrid, Imprenta Alemana, 1913.

Canada Department of Mines: The Production of Cement, Lime, Clay Products, Stone, and other Structural Materials in Canada during the Calendar Year 1912, by John McLeish, B.A., Chief of the Division of Mineral Resources and Statistics. 64 pages, 8vo. Ottawa, Government Printing Bureau, 1913.

U. S. Bureau of Mines: Technical Paper 54, Errors in Gas Analysis due to Assuming that the Molecular Volumes of all Gases are Alike, by George A. Burrell and Frank M. Seibert. 16 pages, 8vo. Washington, Government Printing Office, 1913.

U. S. House of Representatives, 63rd Congress, 2nd Session, Report of the Committee on Mines and Mining on Radium. 18 pages, 8vo. Washington, Government Printing Office, 1914.

An Experiment in the Compilation of Mortality Statistics, by Louis I. Dublin, Statistician, Edwin W. Kopf, Chief Clerk Statistical Bureau, Metropolitan Life Insurance Company, New York. 9 pages, 8vo. Reprinted from the Quarterly Publications of the American Statistical Association, December, 1913.

The Full-time Health Officer and Rural Hygiene, Address delivered at the Conference of State Health Officers, Louisville, Ky., December 8, 1913, by Louis I. Dublin, Ph.D., Statistician Metropolitan Life Insurance Company. 8 pages, 8vo. New York, 1913.

Possibilities of Reducing Mortality at the Higher Age Groups, Read before the Section on Vital Statistics, American Public Health Association, Colorado Springs, September, 1913, by Louis I. Dublin, Ph.D., Statistician Metropolitan Life Insurance Company, New York, 1913. 10 pages, 8vo.

CURRENT TOPICS

An Electric High School.—Electricity from a government power-house furnishes heat for the new high school at Rupert, Idaho, in the centre of the Minidoka Irrigation Project, according to a statement just issued by the United States Bureau of Education. This is said to be the first case on record where a large building has been heated entirely by electricity. The use of electric current for heating and for a variety of other purposes in the new building has caused it to be known as "The Electric High School."

The system of electric heating installed in the Rupert High School is remarkable for its simplicity. The usual arrangement of hot-air pipes, flues, etc., has been adhered to, but instead of furnaces or steam coils a battery of electric heat units, similar to those used in electric baking ovens, provides the heat. Twenty 18-kilowatt units are installed in pairs, each pair with a separate control of the current from a switchboard in the principal's office. Thus the principal can regulate absolutely the amount of current used. An emergency switch in the principal's office may also be used to cut out all current from the entire building—heat, light, power, etc.

Electricity is put to work everywhere in the Rupert building. A 10-horsepower motor, besides driving the ventilating fan, supplies all the power needed for the lathes and saws in the manual training department. An electric water heater supplies the hot water for the domestic science department, for the shower baths, for the various lavatories, and for the science rooms. In the domestic science room each girl of a class of 20 has her individual electric disc stove and all necessary cooking utensils. This room will also have an electric range and other electric equipment for serving cafeteria lunches on a large scale.

In the science laboratories electric hot plates are provided for evaporation purposes, and each pupil will have an electric appliance to take the place of Bunsen burners.

The electric lighting system includes an auditorium set with stage lights and switch control equal to those of the best theatres. The lighting and other equipment have been planned with the idea of making the high school building a model "community centre."

The entire electric equipment was planned by local electricians with the assistance of U. S. Government engineers on the Minidoka Project. The government supplies surplus current from its own power-house, 14 miles above Rupert, at a cost low enough to compete with coal. It is estimated that the cost of heating the new high school by electricity will be $1760 per year. Coal might have been used at a cost of about $1000, but the use of electricity saves

the wages of a fireman at $75 per month, and the cost of installing the electric system was $3000 less than for any other system of heat—the interest on this investment being saved annually. It is therefore believed that the use of electric heat in the Rupert High School, besides being a great convenience, will prove a real economy.

Theory of Vulcanization. D. SPENCE and J. YOUNG. (*Kolloid-Zeits.*, xiii, 265.)—Further experimental evidence is given in support of the author's view that vulcanization is a chemical process. It is shown that there is no "critical temperature": Vulcanization takes place at all temperatures, and the acceleration due to rise of temperature is of the same order as in other chemical reactions. Comparative experiments with caoutchouc, balata, and gutta-percha showed that they all yield the same final product, containing 32 per cent. of combined sulphur and exhibiting the same physical properties. The differences between raw caoutchouc, balata, and gutta-percha must, therefore, be of a physico-chemical nature, and in accord with this view is the fact that as balata and gutta-percha become vulcanized they first acquire more and more the elastic properties of rubber; as vulcanization progresses the properties of the products gradually become more alike, until finally in all three cases a product having the characteristic properties of hard rubber is obtained.

Glass Containing Copper. A. GRANGER. (*Comptes Rendus*, clvii, 935.)—The glasses studied were those found in commerce having an acidity of 2.5 to 3.5 silicic acid. Blue is developed with high alkali content, as in glass of the formula: 0.75 sodium oxide, 0.25 calcium oxide, 0.05 copper oxide, 2.5 to 3.5 silicic acid, the acidity having no appreciable influence on the color within the limits assigned, except that lower silica content tends to allow a surface deposition of metallic copper when the melt is run into a cold metal mould. This reduction to metal by rapid cooling is incidentally suggested as a method of obtaining copper-red. Replacement of calcium oxide in the above formula by lead oxide, zinc oxide, barium oxide, or magnesium oxide does not affect the blue tint, but magnesium oxide is considered unsuitable for the manufacture of glass. Potassium oxide may be substituted for sodium oxide. Aluminum oxide may be added up to 0.1 equivalent, but above that amount produces a greenish glass. Boric acid also tends to give a green coloration and renders the glass less transparent; it is stated that boric glass some millimetres thick is almost opaque. If the alkali content of a blue glass be reduced, and the heavier oxides increased, the blue proportionately decreases and the tendency to green increases. Increase of copper oxide above 0.05 acts in the same way. The production of a green without a trace of blue, however, is difficult within the commercial limits of possibility unless iron oxide be added. A formula for such a glass is: 0.7 Na_2O, 0.15 CaO, 0.15 CuO, 0.0 to 0.25 Al_2O_3, 1.0 B_2O_3, 2.5 SiO_2.

Third Annual Mining Exhibition, under the auspices of the Chemical, Metallurgical, and Mining Society of South Africa, will be held in the Volunteer Drill Hall, Johannesburg, beginning May 19th, and closing May 29th.

The scope of the exhibition will be on much the same lines as in previous years,—*i.e.*, chemical, metallurgical, and mining apparatus and devices for laboratories, works, and mines; models of apparatus for similar purposes; plans, diagrams, etc., of mines, works, plants, machinery, and apparatus; safety and rescue apparatus and appliances; and specimens of crude and manufactured mineral or other natural products of South Africa.

The exhibition is primarily for the benefit and information of those engaged and interested in mining work and mineral products.

No charge will be made for the exhibition of natural products by farmers or prospectors, or for models or apparatus exhibited by mine employees or inventors.

Commercial firms desirous of exhibiting machinery, apparatus, etc., will be charged for the space occupied.

The usual arrangements for exhibitions with regard to customs duties and railway rates will be made.

Further information may be had by applying to Fred Rowland, Secretary, Johannesburg, South Africa.

International Exposition of the Book Industry and Graphic Arts.—An exhibition of the book-making industries will be held in Leipzig, Germany, from April to November of the present year, to commemorate the 150th anniversary of the founding of the Royal Academy for the Graphic Arts.

Lithography, photography, wood carving, stereotyping and electrotyping, printing processes, bookbinding, and all other branches of the graphic arts will be included.

The exhibits will be divided into sixteen groups, consisting of sixty-three classes. Considerable space will be devoted to the department of education, where plans and models of school buildings will be shown, as well as drawings, examination papers, and other work by students.

Detailed information may be had by addressing the management.

Structure of Diamond. W. H. BRAGG and W. L. BRAGG. (*Nature,* xci, 557.)—The new methods of investigation were applied, involving the use of X-rays to the case of the diamond, and there was obtained a knowledge of its structure, which is extremely simple: Each carbon atom has four neighbors at equal distances from it and in directions symmetrically related to each other. The directions are perpendicular to the four cleavage or (1.1.1.) planes of the diamond, therefore parallel to the four lines which join the centre of a given regular tetrahedron to the four corners. The elements of the whole structure are four directions and one length, this

being 1.52×10^{-8} cm. If the structure is observed along a cleavage plane, it is seen that the atoms are arranged in parallel planes containing equal numbers of atoms, but separated by distances which alternate and are in the ratio of 3 : 1 (viz., 1.52 and 0.51 each $\times 10^{-8}$ cm.). It is a consequence of this arrangement that no second-order spectrum is reflected by the (1.1.1.) planes, although spectra of the first, third, fourth, and fifth orders are found. It was this fact that suggested the structure here described. Several tests may be applied and all are satisfied. Zincblende appears to have the same structure, but the (1.1.1.) planes contain alternately only zinc and only sulphur atoms. In this way the crystal acquires polarity and becomes hemihedral.

Paper Dust Explosion. ANON. (*Times. Eng. Suppl.*, Déc. 3, 1913, 24.)—Much interest has been aroused in France by M. Bonn's report on an explosion of paper dust which occurred at a factory at Lille in May last. Although similar explosions of carbonaceous dusts, such as flour, sugar, starch, and cork, have been recorded in France and elsewhere, this appears to be the first occasion in which it has occurred with paper dust. At the factory referred to the edges of paper rolls are ground, and the resulting dust is collected in a dust chamber which is periodically emptied. The explosion occurred when emptying the chamber. A sample of the dust was sent to the experimental station at Liévin and tested, with the result that it was shown to be extremely inflammable, and capable of producing an explosion in a closed space when mixed with air and exposed to flame; the degree of inflammability being equal to that of finely-powdered Liévin coal, containing 30 per cent. of volatile matter.

The Melting-Point of Coal Ash. E. J. CONSTAM. (*Z. Ver. Gas. und Wasserfachmänner in Oesterr. Ung.*, Oct. 15, 1913.)—To determine the fusing-point of ash, equilateral pyramids, obtained by making a paste, moulding and drying, were heated in a tube in an electric furnace. The decrepitation, intumescing, and fusion of the pyramids of ash, and the temperature of fusion, can be optically observed, as the tube, closed at one end, has the properties of an absolutely black body. It appears that: (1) The percentage of ash in a coal has no influence on the melting-point of the ash; (2) the melting-point of the ash is a characteristic of the coal seam; (3) the melting-point of coal ash is in general not affected by coking or the temperature of coking. The investigations gave melting-points ranging from 1150° to 1700° C. (2100° to 3090° F.), and the author classifies coal ash into the following groups, viz., (1) readily fusible—below 1200° C.; (2) fusible—between 1200° C. and 1350° C.; (3) difficultly fusible—between 1350° C. and 1500° C.; (4) very difficultly fusible—between 1500° C. and 1650° C.; and (5) refractory—above 1650° C. Chemical analysis shows that, as regards the samples examined, lime, iron, and sulphur (pyrites) lower

the melting-point, while alumina raises it. Therefore, if an ash is found too readily fusible, the addition of alumina or clay, or the admixture of the coal with another coal having a difficultly fusible ash, should serve to give an ash having the required fusing-point. It is shown that it is necessary also to pay greater attention to the amount of slate in the coal; for, although slate is generally refractory, it becomes the core of large lumps of clinker which interfere with the working of the furnaces. With regard to the uses of coal, the following limits for the melting-point of the ash are named, viz., coke for central heating plant, above 1300° C., anthracite for central heating plant, above 1400° C., boiler coal, above 1400° C.; locomotive and producer coal, above 1500° C.; or fluxing at about 1200° C. Gas coal should have ash with a fusing-point not below 1300° C., and should be as free as possible from pyrites and slate. The author holds the opinion that the determination of the melting-point of the ash will become an important criterion, like the determination of volatile matter and of the proportion of ash, in the valuation of coals, especially gas coals.

The Utility of Airships in the Treatment of Tuberculosis. ANON. (*Sci. Amer.*, cvii, 9, 175.)—Dr. Flemming, a prominent medical authority, at a meeting of the Berlin Aëronautical Association lectured on the beneficial effects of high altitudes on tuberculosis. He pointed out that 15 minutes' exposure to the sun's rays during an airship flight at high altitude meant certain death to the tuberculosis bacilli.

Sugar Cane Grinding. I. H. MORSE. (*Louisiana Planter*, 1, 383.)—To make sugar manufacture profitable in Louisiana under the present conditions, due to the abolition of the sugar duty in the United States, it is advised that the upper part of the cane, which has a much lower sugar content than the middle and bottom parts, should not be ground, but should be used for the production of table syrup, or be utilized as a stock fodder. In Louisiana the cane contains approximately 13.50 per cent. of sucrose in the lower part and 8.0 per cent. in the upper part. By grinding all the cane, the average sucrose content of which is 11.68 per cent., there would be a loss under the new conditions, whereas by crushing only the lower part, which represents about two-thirds of the total weight of the stalk, there would be a profit of about 60 cents per ton.

Action of Hydrogen Peroxide on Aluminum. DROSTE. (*Chem. Zeit.*, xxxvii, 1317.)—Aluminum is slowly attacked by hydrogen peroxide; 0.2 gramme, dissolved in 250 c.c. of a three per cent. solution, in 45 days forming insoluble aluminum hydroxide. No hydroxide remains in colloidal solution; therefore, aluminum vessels are not suitable for liquids which can yield free oxygen or ozone.

Paving Brick from Blast-Furnace Slag. F. G. BOLLES. (*U. S. Consular and Trade Reports, Min. and Eng. World,* Nov. 1, 1913.)—This industry is developed in the north of England, at Middlesborough. The bricks are manufactured by the following process: A suitable site is selected near the blast furnaces, from which a railroad carries the slag to the moulding machine. The car which carries the slag is of plate steel with a firebrick lining, the top is covered over with a removable cap, in the centre of which is a hole about 18 inches in diameter, through which the slag is poured when the car is filled at the furnace. At the bottom of the car is a tap similar to those used on blast furnaces. The car of molten slag is run alongside the wheel carrying the moulds and forming the moulding machine, the trough to the tap extending over the moulds; the clay plug in the tap is knocked out and the molten slag runs into the mould. As soon as it is filled, an operator, by means of a hand-wheel mounted upon a sheet-steel heat deflector and connected through rods and mitre gears to the centre of the moulding wheel, turns the latter so that the next mould comes under the flow of hot slag, and so on till all the moulds are filled. By the time that the wheel has made a quarter revolution the cast bricks have sufficiently cooled so that they may be dropped out of the moulds by knocking off the catch which holds the bottom in place. As soon as they have dropped to the ground they are carried to the adjoining gas-heated annealing furnaces. These furnaces hold approximately 1100 bricks at one charge. The heat retained in the bricks when they are placed in the furnace, together with a very small amount of fuel, again brings them to a cherry red, and as soon as the furnace is filled it is closed and allowed to cool gradually, 24 hours usually being required before the bricks are removed. The capacity of the slag car is approximately 3½ tons, from which 360 to 400 bricks are made. The bricks weigh about 14 pounds each. These bricks are very efficient for street paving, and are being exported to the United States, Canada, and many other countries.

Influence on Life of Tungsten Lamps by Enclosure in Outer Globes. G. SUNDÉN. (*Elektrotechn. Zeitschr.,* xxxiv, 992.)—It is found that the enclosure of tungsten filament lamps within a clear outer globe increases the temperature external to the lamps, and that this may lead to a diminution in useful life. A lamp with an external temperature of 20° C. had a life of 2000 hours, but a similar lamp running in a temperature of 200° C. lived only 40 hours. On the other hand, a water-cooled lamp, with a surrounding temperature of 2.5° C., gave better results, remaining quite clear at the end of the test and showing no diminution in candle-power, whereas the bulbs of the other lamps were distinctly blackened. It is therefore advocated that lamps should not be enclosed in outer globes, especially frosted ones, which materially increase the surrounding temperature.

Quality of Pure Rubber from Various Sources. ANON. (*Bull. Imp. Inst.*, xi, 375.)—*Ceylon.*—Samples obtained from trees tapped at intervals of from three to seven days contained a little more caoutchouc (96.0 to 96.3 per cent., referred to the dry-washed rubber) than those from trees tapped every day or every other day (95.7 or 95.4 per cent. of caoutchouc respectively). *India.*—In six specimens of crêpe rubber from the Mergui District, Burma, the percentages of resin and protein were somewhat higher than is usual in the best plantation Para, and three of the samples yielded an excessive quantity of ash. The two best specimens were of very good quality and contained 94.3 and 93.6 per cent. of caoutchouc respectively (on the dry-washed rubber). *Southern Nigeria.*—Two samples of biscuit rubber from Sapele, Central Province, were satisfactory, both in composition and physical qualities. *British Guiana.*—A sample of biscuit rubber from trees four and one-half to five years old, grown at Issorora, Northwest District, was equal in composition to plantation Para from the East, but was somewhat deficient in strength. When the trees become older the rubber should be of excellent quality. *Papua.*—The rubber exported from Papua up to the present has been obtained from *Ficus Rigo* and an unidentified vine; but there are over 4000 acres planted with *Hevea brasiliensis*, and some of these trees have recently been tapped. A sample of the first consignment of Para rubber, from Sogeri, proved quite equal to the highest grades of plantation Para, both in composition and physical properties.

Sulphur Deposits in New Zealand. ANON. (*Board of Trade Journal*, Nov. 6, 1913.)—Important works in connection with the sulphur deposits of White Island, a mountain top jutting out of deep water in the Bay of Plenty, are to be undertaken, and a company has been formed for this purpose, although operations on the island have been carried on for the past eighteen months. The first shipment of sulphur has been made, which contained 75 to 80 per cent. of pure sulphur. The company expects to have facilities for raising, within the next few months, pure sulphur to the extent of about five hundred tons per month.

Influence of Temperature and Pressure on the Volatility of Zinc and Cadmium. T. K. NAIR and T. TURNER. (*Chem. Soc. Trans.*, ciii, 1534.)—In attempting to remove zinc by volatilization *in vacuo*, on a practical scale, from a charge of about 150 kilogrammes of a zinc alloy, it was found that small imperfections in the vacuum considerably diminished the rate of volatilization. Laboratory experiments with zinc and with cadmium showed that at a given pressure appreciable volatilization does not occur until a definite critical temperature is attained, but from this point the rate of volatilization increases with rise of temperature independent of the initial pressure. A rise of temperature to about 90° C. above that

required for 10 per cent. volatilization will increase the volatilization to 100 per cent. in the same period of time. The critical temperature is raised by gaseous pressure; air has a somewhat greater effect than carbon dioxide, and the latter somewhat greater than hydrogen, but at low pressures the differences are negligible in practice. Down to about 50 mm., each millimetre reduction of pressure causes a small but equal lowering of the critical volatilization temperature, but at lower pressures the effect is much more marked, and when a perfect vacuum is nearly attained a reduction of pressure of one millimetre has an effect 70 times greater than at high pressures. It was observed that zinc is oxidized to a much greater extent by air in motion than by still air.

Conductivity of Copper-Tin Alloys. N. A. PUSCHKIN and A. V. BOSKOV. (*J. Russ. Phys.-Chem. Soc.*, xlv, 746.)—The curves showing the variation of (1) the specific resistance and (2) its temperature coefficient with the composition of copper-tin alloys indicate the existence of a definite compound, Cu_2Sn. The low value of the temperature coefficient, corresponding with the composition Cu_4Sn, indicates the formation, not of a definite compound, but of a solid solution. The addition of tin to copper causes a very rapid increase in the resistance, while copper produces but little change in the resistance of tin.

Early Iron Manufacture in Staffordshire. T. TURNER. (*Engineering*, xciii, 643.)—The analysis of a "ham-bone" from the Little Aston forge showed no graphite, 0.31 per cent. combined carbon, 0.05 per cent. silicon, 0.31 per cent. phosphorus, 4.93 per cent. sulphur, and no manganese. The high sulphur and low carbon and silicon are noteworthy in a metal which was made at least two centuries ago. The probable method of manufacture is also described.

French Hydro-aëroplane Experiments. ANON. (*Sci. Amer.*, cvii, 9, 175.)—During the recent manœuvres of the French fleet in the Mediterranean, the warship *Foudre* was fitted out to carry hydro-aëroplanes. This is easier to accomplish than in the case of ordinary aëroplanes, as there is no launching platform needed from which the fliers start. An overhead crane on the vessel takes up the fliers as they leave the hangar and drops them overboard. The first Nieuport monoplane of this kind, piloted by Ensign Delage, was quite successful. It is of the three-phase type and carries a 100-horsepower Gnome motor. On one occasion the aëroplane went overboard in rough water, and made several flights above the fleet. One part of the fleet represented the enemy in the manœuvres, and the aëroplane observed its position and brought back a very correct report. Some of the flights with one passenger aboard lasted for three hours, flying above Toulon and the harbor and along the coast.

Corrosion of Nickel, Chromium, and Nickel-Chromium Steels. J. N. FRIEND, J. L. BENTLEY, and WALTER WEST. (*Engineering*, xciii, 753.)—Disks were prepared of carbon steels, to serve as standards, of nickel steels, of chromium steels, and of nickel-chromium steels, each 0.7 cm. thick and 2.8 cm. in diameter. These disks were kept nearly immersed in tap-water for 64 days, in sea-water for 60 days, in 0.5 per cent. sulphuric acid for 60 days, in 0.5 per cent. sulphuric acid for 53 days, and they were exposed to alternate wet and dry tests for 52 days. The acceleration tests in 0.5 per cent. sulphuric acid gave misleading results, and the two standard steels, which showed practically equal corrosion in all the other tests, showed 100 per cent. deviation with 0.5 per cent. sulphuric acid, and with the other steels there were remarkable differences. In some cases there were indications of galvanic action in the chromium and nickel steels in the acid tests, and no chromium nor nickel passed into solution, showing that these elements were the constituents of the cathode. The resistance of chromium steels to corrosion in salt water suggests the use of this metal for ship-building. Nickel steels show marked resistance both to acid and neutral corrosive solutions, the resistance increasing with increased nickel content.

New Method of Fermentation of Beetroot Juices and Molasses. MARTINAUD. (*Bull. Assoc. Chemi. Sucr.*, xxxi, 29.)—In the manufacture of alcohol from beetroots, the juice is commonly acidified with sulphuric acid prior to fermentation, in order to check the development of foreign organisms. The author recommends the use of sulphurous acid instead of sulphuric acid. If beet juice is treated with sulphurous acid (*e.g.*, 0.53 gramme SO_2 per litre), and yeast is added, fermentation commences rather slowly, because most of the acid remains in the free state. If, however, the sulphited juice is mixed with about one-third of its volume of juice already in vigorous fermentation, a rapid and satisfactory fermentation of the whole is ensured. A part of the juice fermented in this way may be used for starting fermentation in fresh sulphited juice; the yeast remains pure and may be employed for successive fermentations without further treatment. The same procedure may be applied to the fermentation of molasses.

Electrolysis of Iron and Lead in the Soil. GIROUSSE. (*Comptes Rendus*, clvii, 705.)—Electrodes of iron and lead were placed in wooden boxes coated with paraffin wax and filled with earth kept moist; with the circuit open, there was a difference of potential of 0.15 to 0.2 volt from the lead to the iron. Corrosion of both metals began when the current passed, and its extent was proportional to the quantity of electricity passing and independent of the potential difference. The contact resistance between lead and soil was much greater than that between iron and soil, and under given conditions iron was corroded much more rapidly than lead.

Formation of United States National Radium Institute. C. L. PARSONS. (*U. S. Bureau of Mines*, Oct. 23, 1913.)—Dr. James Douglas and Dr. Howard A. Kelly, of Johns Hopkins University, Baltimore, have bought 27 claims of mining land in Paradox Valley, Col., the greatest radium-bearing ore deposit now known. A National Radium Institute has been formed by the above and others to work the carnotite deposits on the claims under the supervision of the Bureau of Mines, which is said to have devised a new and cheaper method of extracting radium chloride. None of the radium extracted will be for sale, but the whole will be used in special clinics for the treatment of cancer in the Memorial Hospital, New York City, and in Dr. Kelly's hospital in Baltimore.

Corrosion and Preservation of Metals. F. LYON. (*Steamship*, XXV, 322.)—Corrosion, the chemical decomposition of metal, is due to difference in electric potential between the metal and the liquid that wets the surface. Metals that are absolutely dry do not corrode. The state of internal stress of material depending on the mechanical work and heat treatment it has received influences the manner and rate of its corrosion; the more seriously stressed material corrodes more rapidly. A bent plate or angle corrodes more rapidly in and near the bend than the straight portion. Tubes corrode more rapidly at the bends and flanges. Whereas copper alloy castings seldom give trouble, they greatly increase the rate of corrosion of less electro-positive material, such as steel, if in good metallic contact with it. It is customary in such places to secure plates of zinc to the steel in order to protect it. The writer fails to see the value or necessity of this practice for the following reasons: (1) The zinc corrodes rapidly and becomes covered with a coating of zinc oxide, which is always found to be electro-negative to steel; (2) in no case has he found steel connected to zinc corrode less in thirty days than when not so connected; (3) a proper coat of paint between the alloy and steel surfaces will give efficient protection.

Galvanizing, electroplating, and other such processes as means of protection to steel when continuously immersed are dangerous, and not to be recommended. It is deemed sufficient to provide the most homogeneous material possible, both chemically and physically, and to paint it in a proper manner. The painting of metal is discussed. With regard to boilers, condensers, etc., it has been definitely proved that any water showing 3 per cent. alkalinity with calcined sodium carbonate is non-corrosive to steel up to 422° F. If the alkalinity falls to from 1.8 to 2.5 per cent., bad pitting ensues. Much more harm is done by attempts to produce the correct amount of alkalinity in waters than by the small amount of acids which may ever enter an average boiler. The Cumberland method of preserving the interior surfaces of water-carrying pipes and circulating systems, by raising the potential of the water to a value higher than at any point in the system, appears to be the only practicable method, and gives excellent results when properly installed and attended.

Surface Combustion. JAMES A. SEAGER. (*Steam*, xiii, 43.)—It is interesting to note that this system is being applied to a considerable number of industrial processes by the Bonecourt Surface Combustion, Ltd., of Westminster, London, England. Porous diaphragms of refractory material, through which the gas and air are passed, the gas burning without flame, are now used for such purposes as boiling sugar solutions, heating the dies used in cable factories, drying the varnish and stampings used for electrical machinery, and other purposes. For cases where the boiling of solutions or similar operations are required, the Bonecourt diaphragm is in itself far more efficient than any other gas heating device. It is stated that the consumption of gas is reduced by over 50 per cent., as compared with other methods.

For example, a well-known firm of confectionery manufacturers in London has employed these diaphragms in its works for boiling and concentrating sugar solutions, and has thereby effected a saving of more than half of the gas previously required for the same operations. Furthermore, the cleanliness, safety, and ease of operation of this method of heating are great improvements over existing practice. These diaphragms are made in circular or square form, in sizes ranging from 4 inches to 13 inches, while strip formations are made in 6 inches by 3 inches, 10 inches by 8 inches, and 12 inches by 3 inches. In order to supply the required air under pressure, a fan is installed giving a delivery pressure of about 6 inches water gauge, the pressure at the diaphragms being from 2 inches to 3 inches water gauge. Any of the standard fans used for blowing forges, etc., are suitable for this purpose, and the adjustment for obtaining the correct proportion of gas and air at the diaphragm is simple. In order to effect the preliminary heating of the diaphragms, a by-pass is taken off the gas supply; this by-pass is shut off directly the flameless combustion is started. The Bonecourt diaphragms reach their full heat within a few seconds of lighting up, and soon become cold after the gas supply is shut off. By this system of combustion, in which the gas is burnt without flame, over 70 per cent. of the heat contained is converted into radiant energy at the surface of the diaphragm. This is the secret of the high efficiency secured, as it is well known that the gas flame is an efficient medium for heating metallic surfaces, such as the vessels in which solutions are to be boiled, owing to the insulating layer of cool air which forms between the flame and the surface of the vessel. In the case of the diaphragm, a large percentage of radiant heat is quickly absorbed by the vessel and is transferred with high efficiency to the liquid to be heated.

Safety in Railroad Shops. ANON. (*Railway Master Mechanic*, xxxviii, 77.)—In September, 1910, the Pennsylvania Railroad employed the experts of one of the large accident liability insurance companies to make a thorough inspection of each shop plant. In consequence, it was deemed advisable to make the work of safety

inspection a permanent feature and organize a safety movement to cover road and yard as well as shop conditions over the entire system. Safety committees were appointed in January, 1911, for each superintendent's division, and for each shop for repairing engines and cars. These committees have made 17,333 formal recommendations, 13,861 having been complied with at a cost of $413,525.23. During the six months ended June 30, 1913, 3209 safety recommendations were made, 2390 being complied with at a cost of $75,361.97.

In addition to the divisional safety committees, a mechanical engineer was engaged for the specific purpose of making inspections at the various shops. During the year ended June 30, 1913, 58 general inspections and 15 special inspections were made. Usually the first inspection results in attention being called to all hazards, and the following inspections are made to see that the recommendations for the installation of safety devices are complied with.

One of the results of all this detailed attention to safety is that $99,753 has been spent for safety guards—mainly in shops. Practically all machines and dangerous conditions are now guarded. But the real result is that serious accidents to shop employes have been reduced from 5.4 per 1000 employes in 1911 to 3.2 in 1912. In 35 out of 46 shops, where more than 500 men are employed, the number of serious accidents per 1000 men has been reduced by from 5 to 70 per cent.

International Electrical Exhibition, Barcelona, 1915.—An exhibition of electric industries will be held in Barcelona in 1915. The Spanish Government has given the enterprise its official sanction, and has promised financial support. The municipality and other organizations in Barcelona have guaranteed important subsidies. Two millions of dollars have been promised by the Town Council. There is certain to be great activity in the Spanish electrical industries during the next two years. Power stations for the development of electricity in the waterfalls of the Pyrenees and elsewhere are being erected. It is expected that by the time of the opening of the exhibition, 300,000 horsepower will be transmitted to Barcelona, and will be obtainable, for commercial purposes, at very low rates.

PRESS OF
J. B. LIPPINCOTT COMPANY
PHILADELPHIA